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(54) **REFINING METHOD FOR HEAVY OIL**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a refining method for a heavy oil which refines a low-cost heavy oil and is simple, reliable, and economically excellent.

SOLUTION: The raw material oil for this method is a heavy oil with a hydrogen content of 12 wt.% or lower. After the oil is subjected to solvent extraction so as to increase the hydrogen content by 0.2 wt.% or higher, the oil is hydrogenated so as to further increase the hydrogen content by 0.5 wt.% or higher, thus giving a refined oil.

10 **LEGAL STATUS**

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CLAIMS

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[Claim(s)]

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[Claim 1] It is the purification approach of heavy oil of obtaining refined oil by processing including the solvent extraction process which carries out solvent extraction processing of the stock oil, and obtains extracted oil, and the hydrorefining process which carries out the hydrogen treating of the obtained extracted oil to the bottom of existence of hydrogen and a catalyst, and obtains refined oil. A hydrogen content is heavy oil not more than 12wt%, and stock oil introduces the stock oil into a solvent extraction process. a hydrogen content -- stock oil -- receiving -- more than 0.2wt% -- with the solvent extraction process which carries out solvent extraction processing and obtains the deasphaltene oil (DAO) which is extracted oil so that it may increase a deasphaltene oil -- a hydrorefining process -- introducing -- a hydrogen content -- a deasphaltene oil -- receiving -- more than 0.5wt% -- the purification approach of the heavy oil characterized by having the hydrorefining process which carries out hydrorefining and obtains refined oil so that it may increase.

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[Claim 2] It is the purification approach of heavy oil of obtaining refined oil by processing including the solvent extraction process which carries out solvent extraction processing of the stock oil, and obtains extracted oil, and the hydrorefining process which carries out the hydrogen treating of the obtained extracted oil to the bottom of existence of hydrogen and a catalyst, and obtains refined oil. A hydrogen content is heavy oil not more than 12wt%, and stock oil introduces the stock oil into a solvent extraction process. a hydrogen content -- heavy oil -- receiving -- more than 0.2wt% -- with the solvent extraction process which carries out solvent extraction processing and obtains the deasphaltene oil (DAO) which is extracted oil so that it may increase It has the hydrorefining process which carries out hydrorefining and obtains refined oil so that it may increase. a deasphaltene oil -- a hydrorefining process -- introducing -- a hydrogen content -- a deasphaltene oil -- receiving -- more than 0.5wt% -- the hydrogen content obtained at a hydrorefining process -- stock oil -- receiving -- more than 0.7wt% -- the purification approach of heavy oil that the hydrogen content of the refined oil which increased is characterized by being more than 11.5wt%.

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[Claim 3] The purification approach of the heavy oil of claims 1 or 2 that the increment in the hydrogen content to the stock oil of the deasphaltene oil obtained at a solvent extraction process

5 is 0.2 - 1.5wt%, and the increment in the hydrogen content to the deasphaltene oil of the refined oil obtained at a hydrorefining process is 0.5 - 1.5wt%.

10 [Claim 4] The purification approach of the heavy oil of claim 1-3 given in any 1 term that the hydrogen content of said stock oil is 11 - 12wt%, the increment in the hydrogen content to the stock oil of the deasphaltene oil obtained at a solvent extraction process is 0.2 - 1.0wt%, and the increment in the hydrogen content to the deasphaltene oil of the refined oil obtained at a hydrorefining process is 0.5 - 1.0wt%.

15 [Claim 5] The purification approach of the heavy oil of claim 1-4 given in any 1 term that the hydrogen content of said stock oil is less than [11wt%], the increment in the hydrogen content to the stock oil of the deasphaltene oil obtained at a solvent extraction process is 0.5 - 1.5wt%, and the increment in the hydrogen content to the deasphaltene oil of the refined oil obtained at a hydrorefining process is 0.6 - 1.5wt%.

20 [Claim 6] The purification approach of the heavy oil the publication of claim 1-5 given in any 1 term in which the total quantity of nickel and V in said deasphaltene oil carries out solvent extraction processing by 70 or less wtpm so that KONRADSON carbon residue may become less than [15wt%].

25 [Claim 7] The purification approach of the heavy oil of claim 1-6 given in any 1 term that the content of V+nickel of the refined oil processed and obtained at the solvent extraction process and the hydrorefining process is 2 or less wtpm, a KONRADSON carbon residue content is less than [1wt%], and a sulfur content is less than [0.5wt%].

30 [Claim 8] The purification approach of the heavy oil of claim 1-7 given in any 1 term that the hydrogen content in the pyrolysis stock oil is more than 12.0wt% while using said a part of refined oil [at least] as pyrolysis stock oil for low-grade olefin manufacture.

35 DETAILED DESCRIPTION

[Detailed Description of the Invention]

40 [0001]

[Field of the Invention] This invention relates to the purification approach of heavy oil that the refined oil also suitable for the raw material for low-grade olefin manufacture can be obtained from the heavy oil which was not used for the raw material for low-grade olefin manufacture, conventionally especially about the purification approach of the heavy oil by solvent extraction processing and hydrorefining processing in which the impurity of the crude oil origin is efficiently removable.

[0002]

50 [Description of the Prior Art] Since the impurity originating in the origin exists in a crude oil, the petroleum product which uses a crude oil as starting material performs various kinds of physical

5 or chemical purification processings including ordinary pressure and vacuum distillation separation, and is produced. Generally a petroleum fraction, i.e., the distillate separated from the overhead by distillation, has few above-mentioned impurities, and it is used from an impurity being removable by easy purification processing as high-class fuel oil, the raw materials for petrochemistry, etc., such as motor fuel which is the petroleum product of high quality from
10 which the impurity was removed highly, and a gas turbine fuel.

[0003] On the other hand, about heavy oil, such as gas oil, an impurity is condensed, the amount exists with the gestalt which many [not only], but is very hard to be removed, and a limitation is in the impurity removal by hydrorefining which is a fundamental purification means. When
15 refining especially to altitude, the severe reaction condition of an elevated temperature and high pressure is required under existence of hydrogen and a catalyst, and a lot of hydrogen and catalysts are consumed, and a large amount of investment also including an installation cost is needed, and the present condition is that is not economical. Therefore, from heavy oil, added value is high, namely, it looks forward to the method of obtaining that it is simple and
20 economically the quality refined oil from which the impurity was removed by altitude.

[0004] Quality refined oil has the use as a raw material for petrochemistry as one of the application of the. Although *****, such as ethane and naphtha, are manufactured by the pyrolysis as raw materials with main low-grade olefins which are the basic matter of a
25 petrochemical field, such as ethylene and a propylene, the fraction with heavy light gas oil, vacuum gas oil, etc. is also partly used also as a raw material. Although the ethylene plant which used the former ethane as the raw material is in use in the U.S. and the Middle East where natural gas is abundant and cheap, in Japan where naphtha is cheaper, Asia, and Europe, it is using the latter naphtha as a raw material in most cases.

30 [0005] Since it increases more than the case where generation of by-products, such as tar and a pitch, uses ethane as a raw material, caulking by pyrolysis tubing which is a main reaction machine, and the quenching heat exchanger of the latter part, and the correspondence to fouling are needed in the ethylene plant which used naphtha as the raw material. And molecular weight
35 is larger than naphtha and the vacuum gas oil with many metals and sulfur contents is considered to be the limitation in which commercial operation is possible as a raw material of an ethylene plant.

[0006] On the other hand, if stock oil heavier than a gas oil fraction can be used as a raw material
40 for low-grade olefin manufacture from a viewpoint of the amount of feeding, and raw material cost, while raw material cost is cheap, the problem on adequate supply of the stock oil accompanying heavy-izing of petroleum resources can also be solved, and it will become a very big contribution on industry.

45 [0007] It is what offers the approach of collecting the high refined oil of added value from the heavy oil which it succeeds in this invention in view of the above-mentioned situation, and contains the impurity of the crude oil origin by high concentration economically. By carrying out purification processing of the heavy oil, such as ordinary pressure residue made conventionally unsuitable especially as a raw material for low-grade olefins, by the easy and positive approach,
50 it is offering the purification approach of heavy oil the refined oil which was economically

5 suitable also for the raw material for low-grade olefin manufacture being recoverable.

[0008]

10 [Means for Solving the Problem] As a result of inquiring wholeheartedly that this invention persons should attain the above-mentioned purpose, a hydrogen content uses the heavy oil not more than 12wt% as a raw material. By processing the deasphaltene oil which processed so that a hydrogen content might be increased more than a constant rate by solvent extraction, then was obtained so that a hydrogen content may be increased more than a constant rate by hydrorefining processing. The impurity in heavy oil could be removed efficiently and a header and this invention were completed for the refined oil of the high quality from which the impurity was removed by altitude being obtained.

20 [0009] Namely, the solvent extraction process which this invention carries out solvent extraction processing of the stock oil, and obtains extracted oil. It is the purification approach of heavy oil of obtaining refined oil by processing including the hydrorefining process which carries out the hydrogen treating of the obtained extracted oil to the bottom of existence of hydrogen and a catalyst, and obtains refined oil. Stock oil A hydrogen content is heavy oil not more than 12wt%, and the stock oil is introduced into a solvent extraction process. a hydrogen content -- stock oil -- receiving -- more than 0.2wt% -- with the solvent extraction process which carries out solvent extraction processing and obtains the deasphaltene oil (DAO) which is extracted oil so that it may increase a deasphaltene oil -- a hydrorefining process -- introducing -- a hydrogen content -- a deasphaltene oil -- receiving -- more than 0.5wt% -- the purification approach of the heavy oil characterized by having the hydrorefining process which carries out hydrorefining and obtains refined oil so that it may increase is offered.

30 [0010] Since the impurity which is hard to be removed by latter hydrorefining by taking this configuration is processed on the conditions which a hydrogen content increases more than a constant rate by solvent extraction beforehand and it processes on the conditions which a hydrogen content increases more than a constant rate according to a hydrorefining process after that, in each purification process independent, the refined oil of the high quality from which the impurity was removed by inestimable altitude can be obtained certainly. this invention person etc. only by carrying out a solvent extraction process and hydrorefining processing simply. By processing by making into an index the hydrogen content of the heavy oil which processes an impurity paying attention to the ability not to carry out certainly, so that the hydrogen content of the specified quantity may be made to increase at a solvent extraction process and the

40 hydrorefining process following it, respectively. It can obtain on the economical conditions at which it finds out that the refined oil from which the impurity was removed by altitude can be obtained, the conditions of a solvent extraction process and a hydrorefining process are not made into a severe condition certainly and efficiently, and the balance of a load is maintained.

45 [0011] Furthermore, the hydrogen content of the refined oil obtained above in this invention offers the purification approach of more than 11.5wt% and the heavy oil with which it is characterized by being more than 12.0wt% preferably. When the refined oil obtained by this is applied to the raw material for low-grade olefin manufacture which is a raw material for petrochemistry, caulking and generating of fouling are suppressed also in the case of a pyrolysis reaction, and the commercial operation of it becomes possible. The purification approach of this

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5 reason to this invention is the approach of having been economically excellent which can obtain the high refined oil of added value certainly and efficiently.

[0012]

10 [Embodiment of the Invention] A hydrogen content processes [by using 10 - 12wt% heavy oil as a raw material] this invention preferably, respectively on less than [12wt%] and the conditions which attain whenever [predetermined purification] in a solvent extraction process and hydrorefining down stream processing, respectively. Generally residue oils, such as ordinary pressure residual oil, super-heavy crude, etc. corresponded, and since high impurity concentration was high, as for the heavy oil not more than 12wt% used for this invention, the application was limited. The hydrogen content of these heavy oil is 9 - 12.5 % of the weight, many are 9 - 11.5 % of the weight, and generally, even if refined conventionally, it was fully unremovable, and it was not used for the raw materials for petrochemistry for low-grade olefins etc., the impurity having been used as unsuitable.

20 [0013] this invention -- a hydrogen content -- the heavy oil not more than 12wt% -- stock oil -- carrying out -- as the 1st process -- solvent extraction processing -- carrying out -- a hydrogen content -- more than 0.2wt% -- the deasphaltene oils which are the extracted oil which increased are collected. In this solvent extraction down stream processing, a part for an asphaltene with few hydrogen contents is removed alternatively. The amount of this asphaltene is having micellar structure which hydrogen contents, such as condensed multi-ring aromatic series and a cycloparaffin ring, become from few compounds, the porphyrin compound of metals, such as carbon residue, and V, nickel, contains it in that interior, and it is known that the impurity is condensed. and the amount of asphaltene controls a hydrorefining reaction remarkably, and it also knows promoting degradation of a catalyst -- having -- **** -- this invention -- setting -- a hydrogen content -- more than 0.2wt% -- as a result, the specified quantity of an asphaltene is alternatively removed by carrying out solvent extraction processing on the increasing conditions.

35 [0014] Solvent extraction processing can apply solvent deasphalting processing in which it is known conventionally, and divides it into a deasphaltene oil and the asphaltene by which there are few hydrogen contents and metal and carbon residue are condensed by carrying out counterflow contact of the heavy oil with the solvent of C3-C5 in a solvent extraction column. and the thing for which the amount of solvents to the class and heavy oil of a solvent to be used and extract temperature conditions are chosen suitably -- a hydrogen content -- more than 0.2wt% -- extract processing conditions can be controlled and the extracted oil of this invention can be obtained so that it may increase. As a solvent of C3-C5, as being chosen out of a propane, butane, and a pentane, one is preferably used as it is few.

45 [0015] Deasphaltene oils can be collected from the overhead section of an extraction column as an extract with a solvent, and the solvent in an extract can be obtained by carrying out separation removal in the state of supercritical. About an asphaltene, these is collected from the bottom section as raffinate with some solvents, and the solvents in raffinate are collected by evaporation. [0016] the hydrogen content of the deasphaltene oil obtained by this solvent extraction down stream processing in this invention -- the hydrogen content of raw material heavy oil -- more than 0.2wt% -- it is increasing. furthermore, 0.2 - 1.5wt% -- increasing -- desirable -- 0.2 -

5 1.2wt% -- especially the thing to increase is desirable.

10 [0017] Furthermore, it is desirable to change the augend of the hydrogen content of solvent extraction processing with the value of the hydrogen content of raw material heavy oil. That is, when the hydrogen content of stock oil is more than 11wt%, in a solvent extraction process, it is desirable to control extract processing conditions to stock oil to become 0.2 - 0.5wt% of increment in a hydrogen content especially 0.2 - 1.0wt%. Moreover, if a hydrogen content is less than [11.0wt%], the augend of the range of 0.5 - 1.5wt%, especially 0.8 - 1.3wt% is desirable.

15 [0018] Since removal of an impurity fully becomes impossible even if it becomes inadequate removing [of the asphaltene which is an impurity as it is less than / 0.2wt%] the increment in the hydrogen content in a solvent extraction process and it processes it at a latter hydrorefining process, they are indispensable conditions. although it is better on the other hand as the upper limit of the augend is large from a viewpoint of whenever [purification] -- more than 1.5wt% -- since the recovery of a deasphaltene oil falls in making it increase, it is not economical.

20 [0019] this invention -- the above-mentioned solvent extraction processing -- a hydrogen content -- more than 0.2wt% -- hydrorefining processing of the deasphaltene oil which carried out solvent extraction processing so that it might increase is carried out as the 2nd continuing process. hydrorefining processing of this invention -- setting -- a hydrogen content -- more than 25 0.5wt% -- it processes on the increasing conditions. This hydrorefining processing is typical purification processing which processes a hydrocarbon with elevated-temperature high pressure under existence of a catalyst and hydrogen, and can include all the reactions, such as hydrocracking, hydrodesulfurization, hydrogenation demetallization, and hydrogenation denitrification. Namely, the sulfur compound in hydrocracking which obtains low-molecular-weight refined oil from raw material heavy oil, and a hydrocarbon is made to react with 30 hydrogen. Hydrodesulfurization which dissociates by making it a hydrogen sulfide and obtains the refined oil of low-sulfur concentration from stock oil, Hydrogenate the metallic compounds which are in a hydrocarbon under elevated-temperature high-pressure hydrogen, make it an element-like metal, and deposition is carried out on a catalyst. The nitride in a hydrocarbon may 35 be made to react with hydrogen under the hydrogenation demetallization which obtains the refined oil of low metal concentration, and elevated-temperature high-pressure hydrogen, and you may dissociate by making it ammonia, and may also include all the reactions, such as hydrogenation denitrification which obtains the refined oil of low nitrogen concentration from stock oil.

40 [0020] Although a sulfur content, a metal, etc. are contained in heavy oil as an impurity, since removing only at a hydrorefining process beforehand by solvent extraction down stream processing of the preceding paragraph has removed the difficult impurity, an impurity can be efficiently removed to low concentration, without making it a severe condition. It is desirable to 45 use as a catalyst used for hydrorefining processing of this invention combining at least two kinds chosen from a hydrogenation demetallization catalyst, a hydrodesulfurization catalyst, a hydrodesulfurization demetallization catalyst, and a hydrocracking catalyst. It is the Co/Mo, nickel/Co/Mo, and nickel/Mo system preferably as a catalyst used for hydrorefining.

5 [0021] Although there is especially no limit in the conditions of a hydrotreating reaction, the
range of the hydrotreating reaction condition currently generally performed is desirable. That is,
a hydrogen partial pressure has desirable 60-150kg/cm², and especially its 80-130kg/cm² is
desirable. Moreover, hydrogen / oil ratio has desirable 400-1200Nm³/kl, and especially its 600-
1000Nm³/kl is desirable. 1.0 [0.1-]/hr of LHSV is desirable, and 0.8 [0.2-]/especially its hr is
10 desirable. 340-440 degrees C of reaction temperature are desirable, and especially its 350-420
degrees C are desirable.

[0022] these conditions -- the general conditions of hydrotreating -- it is -- this invention --
setting -- after the solvent extraction process of the preceding paragraph -- a hydrogen content --
15 more than 0.5wt% -- if a hydrotreating process is performed on the increasing conditions, the
impurity as the last refined oil is efficiently removable. In this invention, when the hydrogen
content of stock oil is 11 - 12wt%, as for the increment in the hydrogen content to the
deasphaltene oil of the refined oil obtained at a hydrotreating process, it is especially desirable
that it is 0.5 - 0.9wt% 0.5 - 1.0wt%. Moreover, when the hydrogen content of stock oil is less
20 than [11wt%], as for the increment in the hydrogen content to the deasphaltene oil of the
refined oil obtained at a hydrotreating process, it is especially desirable that it is 0.8 - 1.3wt% 0.6
- 1.5wt%.

[0023] Furthermore, it is desirable that it is 0.5 - 1.0wt% augend if the hydrogen content of the
25 deasphaltene oil obtained at the solvent extraction process of the preceding paragraph is more
than 11.5wt%, and if the augend of the hydrogen content in hydrotreating down stream
processing of this invention is less than [11.5wt%], it is desirable [augend] that it is 0.6 -
1.5wt% augend. When impurity removal of a deasphaltene oil becomes it inadequate that the
augend of a hydrogen content is less than [0.5wt%] in hydrotreating down stream processing
30 and it makes it the augend beyond 1.5wt%, it is not economical in order to have to make severe
the processing conditions of hydrotreating reactions, such as a hydrogen partial pressure,
reaction temperature, and a catalyst fill.

[0024] That is, without making a hydrogen partial pressure and reaction temperature extremely
35 high in hydrotreating down stream processing which continues by removing beforehand
alternatively a part for the asphaltene which is the impurity which is hard to be removed by
hydrotreating down stream processing in solvent extraction down stream processing, if it states
from a viewpoint of the reaction condition of hydrotreating, even if it makes the amount of
catalysts increase sharply and does not lengthen reaction time, an impurity can be efficiently
40 removed to low concentration. Consequently, parts for a metal, such as KONRADSON carbon
residue, nickel, V, etc. which exist with the gestalt which condenses and is hard to be removed in
an asphaltene, are alternatively removed by solvent extraction, and, subsequently can remove
intensively impurities, such as metals, such as the sulfur and nickel which exist with the gestalt
which is easy to be removed, and V, by hydrotreating processing.

45 [0025] When applying the refined oil processed at the purification process by above-mentioned
this invention to the raw material for low-grade olefin manufacture and carrying out elevated-
temperature pyrolysis, since the impurity used as the causative agent of caulking or fouling is
reduced certainly and efficiently, it can be applied to commercial production from the yield and
50 continuous-running nature of a low-grade olefin. This means that quality refined oil can be

5 obtained for the heavy oil considered to be conventionally unsuitable as a low-grade olefin raw material, such as a residue oil and super-heavy crude, by purification simple as starting material.

10 [0026] Moreover, in this invention, if it is the refined oil processed on the conditions with which are satisfied of the above, it is effective as refined oil of this invention, but when using as a raw material for low-grade olefin manufacture especially, it is required for a hydrogen content to be more than 11.5wt%, and it is more desirable that it is more than 12.0wt%.

15 [0027] In this invention, it is required for the hydrogen content of the refined oil obtained by solvent extraction and two steps of purification of hydrorefining to increase heavy oil from raw material heavy oil by 0.7% of the weight or more, it is desirable that it is 0.8 - 2.7wt%, and it is desirable that it is further 1.0 - 2.2wt%. Moreover, when using as a raw material for low-grade olefin manufacture, as for the hydrogen content of the last refined oil, it is desirable that it is more than 11.5wt%, and it is still more desirable that it is 12.0 - 13.5wt%.

20 [0028] the hydrogen content of refined oil -- more than 11.5wt% and raw material heavy oil -- more than 0.7wt% -- by performing solvent extraction processing and hydrorefining processing so that it may increase The property in each processing is complemented mutually and does not cover an excessive load over the equipment for the solvent extraction of each process, and hydrorefining. The refined oil refined by altitude can be obtained by high yield, and when it
25 applies to the raw material for petrochemistry, the refined oil which it was hard coming to generate caulking and fouling, and was suitable for the raw material for petrochemistry by high yield can be manufactured.

30 [0029] the process which carries out solvent extraction processing of the heavy oil of this invention -- setting -- the hydrogen content of the stock oil -- more than 0.2wt% -- although extract operation is carried out on the increasing conditions -- a nickel+V metal -- the inside of a residue oil and super-heavy crude -- several -- it is contained 10-thousands wtpm(s). Since these are condensed by the asphaltene, and exist and an asphaltene can be alternatively removed at a solvent extraction process, it is desirable to set especially to 50 or less wtpms 70 or less wtpms
35 of metal concentration of nickel+V in the deasphaltene oil which is extract refined oil about the content in a deasphaltene oil by solvent extraction processing. Moreover, it is desirable less than [15wt%] and that a carbon residue content performs solvent extraction processing so that it may become less than [12wt%] especially. namely, solvent extraction processing -- a hydrogen content -- 0.2wt(s)% -- while making it increase, it is desirable to make nickel+V metal
40 concentration to 70 or less wtpms, and to make KONRADSON carbon residue into less than [15wt%], without making the conditions of latter hydrorefining processing severe by this, an impurity can be removed certainly and the refined oil of high quality can be obtained.

45 [0030] Moreover, it is desirable less than [5wt%] and to make sulfur concentration of a deasphaltene oil into less than [4wt%] especially. the sulfur content of the last refined oil obtained by that cause by the continuing hydrorefining processing -- less than [0.5wt%] -- it can process certainly so that it may become less than [0.3wt%] preferably. the nickel+V concentration of the last refined oil from which 70 or less wtpms and carbon residue concentration are obtained in the nickel+V concentration of a deasphaltene oil by the
50 hydrorefining processing which continues when less than [15wt%] and sulfur concentration

5 consider as less than [5wt%] -- 2 or less wtpmms -- desirable -- 1 or less wtpm and carbon
residue concentration -- less than [1wt%] and sulfur concentration -- less than [0.5wt%] -- it
can process certainly so that it may become less than [0.3wt%] preferably. By making the sulfur
content of the last refined oil into 0.5 or less % of the weight, when it uses as stock oil for low-
10 grade olefins, the corrosion of pyrolysis equipment can be suppressed in the tolerance of an
ingredient, and commercial manufacture of the substantial raw material for low-grade olefins can
be enabled.

[0031] Especially in this invention, it is desirable to perform solvent extraction processing and
hydrorefining processing so that 2 or less wtpmms of nickel+V metal contents of the last refined
15 oil may be set to 1.0 or less wtpmms. By setting a nickel+V metal content to 1 or less wtpm for
the deasphaltene oil with which the nickel+V metal content turned into below the 70 weight ppm
by solvent extraction processing further by hydrorefining, it can reduce caulking remarkably,
refined oil can be obtained by high yield, and the refined oil can be used as a pyrolysis raw
material for low-grade olefin manufacture.

20 [0032] In the industrial method of manufacturing the low-grade olefin containing ethylene and a
propylene by the pyrolysis reaction, the maintenance nature to fouling and olefin yield by
decoking or byproduction heavy oil influence the economical efficiency, and 25% or more of
especially yield of a low-grade olefin serves as a standard. If a low-grade olefin is furthermore
25 seen in detail, 10% or more of propylene yield will become [ethylene yield] a standard 15% or
more.

[0033] Moreover, about fouling by caulking and byproduction heavy oil which influence the
maintenance nature of pyrolysis equipment, it corresponds in periodical decoking and cleaning.
30 In order to prevent too much decomposition, in case it quenches especially the hot
decomposition product disassembled with decomposition tubing about byproduction heavy oil by
down-stream heat exchange, when there are many amounts of generation of heavy oil, it
blockades a heat exchanger and piping, and makes long-term continuous running impossible.
When leaving heavy oil like this invention, the amount of generation of the byproduction heavy
35 oil in a pyrolysis reaction can consider as the standard of commercial operation.

[0034] When the hydrogen content with which the refined oil obtained by this invention is not
conventionally used for raw materials for low-grade olefin manufacture, such as ethylene, carries
out purification processing and offers the heavy oil not more than 12wt% as a raw material for
40 low-grade olefin manufacture, the olefin yield and the caulking property at the time of a
pyrolysis are good, and make industrial production possible.

[0035] When there are few contents of the impurity in the distillate obtained in mere distillation
separation of a crude oil etc. in this invention, or when the content of an impurity can be reduced
45 by easy purification By using a crude oil as a start raw material, it separates into a distillate and a
residue oil, and at least solvent extraction and the part which carried out hydrorefining
processing, considered as refined oil, and carried out hydrorefining of the above-mentioned
distillate to this refined oil can be mixed as mentioned above, and the atmospheric-distillation
residue oil and vacuum-distillation-residue oil which are a residue oil can also be made into

5 refined oil.

10 [0036] In this case, if a solvent extraction process and a hydrotreating process satisfy the increment criteria of the hydrogen content of this invention, by mixing a distillate with few impurity contents, the whole high impurity concentration can be decreased, the amount of supply of refined oil can be made to increase further, and it will become things. When supplying as stock oil for low-grade olefin manufacture, it is further hard coming to generate coking and fouling in a pyrolysis reaction, and they can enable commercial production.

[0037]

15 [Example] Next, although an example is shown and this invention is further explained to a detail, this invention is not limited to the following examples.

20 [0038] the heavy oil (hydrogen content: -- 11.25 [wt%] --) examples 1-4 and the example 1 of a comparison - whose 5 example 1 API gravity are the residue oils of 14.3 nickel+V metal: -- 65 [wtppm] and KONRADSON carbon residue (it is called Following CCR): -- 11.1 [wt%] -- It introduces into a solvent extraction processor by making S:3.95 [wt%] into stock oil. After carrying out extraction separation and obtaining a deasphaltene oil (it is called the following DA 0) so that it may become extractability (solvent/Oil ratio: 8/1) 81wt% using a normal pentane solvent, purification processing of the deasphaltene oil was carried out on the following
25 hydrotreating conditions, and the refined oil 1 of this invention was obtained.
hydrotreating condition: -- nickel/Mo+nickel/Co/Mo catalyst (it is 1/9 at volume ratio), and hydrogen partial pressure:90[atm] H₂ / Oil ratio: -- 600 [Nm³/kl] and temperature: -- 380 degrees C of the augend of the yield to the stock oil of the deasphaltene oil LHSV:0.5 [1/hr] obtained and refined oil 1, a hydrogen content, and the hydrogen content in each process,
30 V+nickel contents, CCR(s), and sulfur concentration are shown in Table 1. The hydrogen content was measured by the CHN elemental-analysis method.

35 [0039] The stock oil used in the example 2 example 1 was introduced into the solvent extraction processor, after carrying out extraction separation and obtaining a deasphaltene oil so that it may become extractability (solvent/Oil ratio: 8/1) 84wt% using a normal pentane solvent, hydrotreating of the DAO was carried out on the same conditions as an example 1, and the refined oil 2 of this invention was obtained. The augend of obtained DAO and the yield to the stock oil of refined oil 2, a hydrogen content, and the hydrogen content in each process, a V+nickel content, CCR, and sulfur concentration are shown in Table 1.

40 [0040] The stock oil used in the example 3 example 1 was introduced into the solvent extraction processor, after carrying out extraction separation and obtaining DAO so that it may become extractability (solvent/Oil ratio: 8/1) 81wt% using a normal pentane solvent, purification processing of the DAO was carried out on the following hydrotreating conditions, and the
45 refined oil 3 of this invention was obtained.
hydrotreating condition: -- nickel/Mo+nickel/Co/Mo catalyst (it is 1/9 at volume ratio), and hydrogen partial pressure:85[atm] H₂ / Oil ratio: -- 600 [Nm³/kl] and temperature: -- 360 degrees C of the augend of DAO LHSV:0.5 [1/hr] obtained and the yield to the stock oil of refined oil 3, a hydrogen content, and the hydrogen content in each process, V+nickel contents,

5 CCR(s), and sulfur concentration are shown in Table 1.

[0041] The stock oil used in the example 4 example 1 was introduced into the solvent extraction processor, after carrying out extraction separation and obtaining DAO so that it may become extractability (solvent/Oil ratio: 8/1) 76wt% using an isobutane / normal pentane mixed solvent, purification processing of the DAO was carried out on the following hydrorefining conditions, and the refined oil 4 of this invention was obtained.
 10 hydrorefining condition: -- nickel/Mo+nickel/Co/Mo catalyst (it is 1/9 at volume ratio), and hydrogen partial pressure: 110[atm] H₂ / Oil ratio: -- 800 [Nm³/kl] and temperature: -- 380 degrees C of the augend of DAO LHSV: 0.3 [1/hr] obtained and the yield to the stock oil of refined oil 3, a hydrogen content, and the hydrogen content in each process, V+nickel contents, CCR(s), and sulfur concentration are shown in Table 1.
 15

[0042]

[Table 1]

| | 原料油 | 実施例 1 | | 実施例 2 | | 実施例 3 | | 実施例 4 | |
|------------------|-------|-----------|-------|-----------|-------|-----------|-------|-----------|-------|
| | | DAO 精製油 1 | | DAO 精製油 2 | | DAO 精製油 3 | | DAO 精製油 4 | |
| 得率 (wt %) | 100 | 81 | 77 | 84 | 79 | 81 | 78 | 76 | 72 |
| 水素含有量 (wt %) | 11.25 | 11.55 | 12.33 | 11.50 | 12.28 | 11.55 | 12.14 | 11.75 | 12.65 |
| 水素含有量増加量 (wt %) | — | 0.30 | 0.78 | 0.25 | 0.78 | 0.30 | 0.59 | 0.50 | 0.90 |
| 合計水素増加量 (wt %) | — | — | 1.08 | — | 1.03 | — | 0.89 | — | 1.40 |
| V+Ni (wt ppm) | 65.0 | 7.3 | <0.1 | 10.7 | <0.1 | 7.3 | <0.1 | 3.7 | <0.1 |
| コークスの残留炭素 (wt %) | 11.10 | 2.60 | 0.41 | 3.20 | 0.62 | 2.60 | 0.76 | 1.80 | 0.21 |
| S (wt %) | 3.95 | 3.35 | 0.06 | 3.45 | 0.16 | 3.35 | 0.26 | 3.19 | 0.02 |

20

[0043] Except having made the rate of solvent extraction into 88% using the same stock oil as example of comparison 1 example 1, after carrying out extraction separation by the same extraction condition as an example 1 and obtaining DAO, hydrorefining of the DAO was carried out on the following hydrorefining conditions, and comparative refined oil A was obtained.
 25 hydrorefining -- conditions -- : -- nickel/Mo+Co/Mo -- a catalyst (it is 1/9 at a volume ratio) -- hydrogen -- a partial pressure -- : -- 90 -- [-- atm --] -- H -- two -- / -- Oil -- : -- 600 -- [-- Nm -- three -- / -- kl --] -- temperature -- : -- 360 -- degree C -- LHSV -- : -- 0.5 -- [-- one -- / -- hr --] -- obtaining -- having had -- DAO -- and -- refined oil -- A -- stock oil -- receiving -- a yield -- a hydrogen content -- each -- a process -- it can set -- a hydrogen content -- augend -- V+nickel -- a content -- CCR -- sulfur -- concentration -- Table 2 -- be shown .
 30

[0044] After carrying out extraction separation and obtaining DAO using the same stock oil as example of comparison 2 example 1 so that it may become extractability (solvent/Oil ratio: 8/1) 86wt% using a normal pentane solvent, purification processing of the DAO was carried out on the following hydrorefining conditions, and comparative refined oil B was obtained.
 35 hydrorefining -- conditions -- : -- nickel/Mo+Co/Mo -- a catalyst (it is 1/9 at a volume ratio) -- hydrogen -- a partial pressure -- : -- 90 -- [-- atm --] -- H -- two -- / -- Oil -- : -- 600 -- [-- Nm -- three -- / -- kl --] -- temperature -- : -- 360 -- degree C -- LHSV -- : -- 0.5 -- [-- one -- / -- hr --] -- obtaining -- having had -- DAO -- and -- refined oil -- B -- stock oil -- receiving -- a yield -- a hydrogen content -- each -- a process -- it can set -- a hydrogen content -- augend -- V+nickel -- a content -- CCR -- sulfur -- concentration -- Table 2 -- be shown .
 40

5 [0045] After having carried out extraction separation, carrying out and obtaining DAO using the same stock oil as example of comparison 3 example 1 so that it may become extractability (solvent/Oil ratio: 8/1) 81wt% using a normal pentane solvent, purification processing of the DAO was carried out on the following hydrorefining conditions, and comparative refined oil C was obtained.

10 hydrorefining -- conditions -- : -- nickel/Mo+Co/Mo -- a catalyst (it is 1/9 at a volume ratio) -- hydrogen -- a partial pressure -- : -- 90 -- [-- atm --] -- H -- two -- /-- Oil -- : -- 600 -- [-- Nm -- three -- /-- kl --] -- temperature -- : -- 345 -- degree C -- LHSV -- : -- 0.6 -- [-- one -- /-- hr --] -- obtaining -- having had -- DAO -- and -- refined oil -- C -- stock oil -- receiving -- a yield -- a hydrogen content -- each -- a process -- it can set -- a hydrogen content -- augend -- V+nickel -- a content -- CCR -- sulfur -- concentration -- Table 2 -- be shown .

15

[0046] Using the same stock oil as example of comparison 4 example 1, extraction separation was carried out and comparative refined oil D was obtained so that it might become extractability (solvent/Oil ratio: 8/1) 45wt% using a propane solvent. The augend of the yield to the stock oil of the obtained refined oil D, a hydrogen content, and the hydrogen content in each process, a V+nickel content, CCR, and sulfur concentration are shown in Table 2.

20

[0047] Using the same stock oil as example of comparison 5 example 1, purification processing was carried out on the following hydrorefining conditions, and comparative refined oil E was obtained.

25 hydrorefining -- conditions -- : -- nickel/Mo+Co/Mo -- a catalyst (it is 1/9 at a volume ratio) -- hydrogen -- a partial pressure -- : -- 150 -- [-- atm --] -- H -- two -- /-- Oil -- : -- 1000 -- [-- Nm -- three -- /-- kl --] -- temperature -- : -- 380 -- degree C -- LHSV -- : -- 0.25 -- [-- one -- /-- hr --] -- obtaining -- having had -- refined oil -- E -- stock oil -- receiving -- a yield -- a hydrogen content -- each -- a process -- it can set -- a hydrogen content -- augend -- V+nickel -- a content -- CCR -- sulfur -- concentration -- Table 2 -- be shown -- .

30

[0048]

[Table 2]

| | 原料油 | 比較1 | | 比較2 | | 比較3 | | 比較4 | 比較5 |
|------------------|-------|-------|-------|-------|-------|-------|-------|----------|-----------|
| | | DAO | 精製油A | DAO | 精製油B | DAO | 精製油C | D (抽出のみ) | E (水素化のみ) |
| 得率 (wt%) | 100 | 88 | 84 | 86 | 82 | 81 | 77 | 45 | 95 |
| 水素含有量 (wt%) | 11.25 | 11.37 | 11.79 | 11.40 | 12.08 | 11.55 | 11.90 | 11.95 | 12.10 |
| 水素含有量増加量 (wt%) | — | 0.15 | 0.42 | 0.15 | 0.68 | 0.30 | 0.35 | 0.70 | 0.85 |
| 合計水素増加量 (wt%) | — | — | 0.54 | — | 0.83 | — | 0.65 | — | — |
| V+Ni (wtppm) | 65.0 | 16.8 | <0.1 | 13.5 | <0.1 | 7.3 | <0.1 | 2.0 | 7.0 |
| コaltar残留炭素 (wt%) | 11.10 | 4.30 | 1.47 | 3.70 | 0.81 | 2.60 | 1.21 | 0.50 | 5.70 |
| S (wt%) | 3.95 | 3.57 | 1.03 | 3.51 | 0.32 | 3.35 | 0.83 | 3.07 | 0.50 |

35

[0049] It pyrolyzed on condition that the following, using respectively the last refined oil obtained in the example examples 1-4 of low-grade olefin manufacture, and the examples 1-5 of a comparison.

40 Reaction condition: Coil : It is use feeding about bore 28mmphi and HPM material ethylene decomposition tubing with a die length of 1440mm (heating unit 1200mm per part). : Stock oil = 1.69 [L/Hr] and water are adjustment reaction temperature about the amount of supply so that it

5 may be set to 1.0 by the weight ratio to stock oil. : 900-degree-C pressure : Ordinary pressure
 residence time : It asked for the yield of the low-grade olefin (ethylene and propylene) obtained
 for 0.5 seconds from the gas presentation in the generation gas analyzed using generation
 capacity and a gas chromatograph. The amount of generation of byproduction heavy oil
 10 calculated the generation oil after cooling cracked gas from the bottom oil quantity after
 separating a naphtha fraction by distillation. Moreover, decision of continuous-running nature is
 a generation weight ratio to stock oil, and judged the byproduction heavy oil leading to fouling
 which deposited in the sudden cooling section which branches from a coil as less than [30wt%]
 =O and more than 30wt%=x. A result is shown in Table 3.

15 [0050]
 [Table 3]

| | 実施例1 | 実施例2 | 実施例3 | 実施例4 | 比較A | 比較B | 比較C | 比較D | 比較E |
|---------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 水素含有量 (wt%) | 12.33 | 12.28 | 12.14 | 12.65 | 11.79 | 12.08 | 11.90 | 11.95 | 12.10 |
| エチレン収率 (wt%) | 16.7 | 16.1 | 15.9 | 18.1 | 11.5 | 13.1 | 13.4 | 13.1 | 14.0 |
| プロピレン収率 (wt%) | 13.1 | 12.5 | 12.2 | 14.8 | 8.5 | 9.7 | 10.2 | 10.1 | 10.4 |
| 副生重質油 (wt%) | 28.1 | 28.7 | 29.5 | 24.5 | 36.5 | 33.2 | 34.8 | 34.6 | 32.9 |
| 連続運転性 | ○ | ○ | ○ | ○ | × | × | × | × | × |

20 [0051] DAO obtained by solvent extraction processing in the examples 1-4 of this invention --
 heavy stock oil -- comparing -- a hydrogen content -- more than 0.2wt% -- the hydrorefining oil
 which extracts so that it may increase, and continues -- DAO -- comparing -- a hydrogen content
 -- more than 0.5wt% -- it increases -- as -- processing -- as a result -- the last refined oil -- heavy
 stock oil -- comparing -- more than 0.7wt% -- it processed so that it might increase. In the refined
 25 oil of this invention, as for V+nickel, the refined oil from which the impurity was removed for
 0.1 or less wtpm and KONRADOSON carbon residue by less than [0.8wt%] and less than [
 sulfur concentration 0.3wt%] was obtained by each. On the other hand, the KONRADOSON
 carbon residue of the last refined oil is more than 0.8wt%, and the sulfur concentration of the
 examples 1-5 of a comparison with which are not satisfied of the increment in the hydrogen
 content of this invention is more than 0.3wt%.

30 [0052] It turns out only especially by solvent extraction processing that sulfur concentration does
 not fall even if it makes extractability of DAO small, and KONRADOSON carbon residue is not
 removable only by hydrorefining processing even if it increases hydrogen consumption sharply.
 Moreover, by the result of having carried out pyrolysis processing of the obtained refined oil,
 35 and having manufactured the low-grade olefin, by the refined oil of this invention, ethylene yield
 all exceeded 15%, propylene yield is over 10% and continuous-running nature was further
 judged to be the possible range from the generation situation of byproduction heavy oil. On the
 other hand, in the example of a comparison with which are not satisfied of this invention,
 ethylene yield does not exceed 15%, but further, there are many amounts of generation of
 40 byproduction heavy oil, and it turns out that each continuous-running nature has a problem.

[0053] It introduced into the solvent extraction processor by making into stock oil the heavy oil
 (hydrogen content: 10.68wt% and nickel+V metal:246wtpm, CCR:25wt%, and S:5.5wt%)
 which is a residue oil of example 5 API gravity 4.2, and after carrying out extraction separation
 45 and obtaining DAO so that it may become extractability (solvent/Oil ratio: 8/1) 63wt% using an
 isobutane solvent, hydrorefining of the DAO was carried out on condition that the following, and

5 the refined oil 5 of this invention was obtained.
 hydrorefining condition: -- nickel/Co/Mo+Co/Mo catalyst (it is 2/8 at volume ratio), and
 hydrogen partial pressure: 110[atm] H₂ / Oil ratio: -- 800 [Nm³/kl] and temperature: -- 380
 degrees C of the augend of DAO LHSV: 0.3 [1/hr] obtained and the yield to the stock oil of
 refined oil 5, a hydrogen content, and the hydrogen content in each process, V+nickel contents,
 10 CCR(s), and sulfur concentration are shown in Table 4.

[0054] After carrying out extraction separation and obtaining DAO using the same stock oil as
 example 6 example 5 so that it may become extractability (solvent/Oil ratio: 8/1) 65wt% using
 an isobutane solvent, purification processing of the DAO was carried out on the following
 15 hydrorefining conditions, and the refined oil 6 of this invention was obtained.
 hydrorefining -- conditions -- : -- nickel/Mo+Co/Mo -- a catalyst (it is 2/8 at a volume ratio) --
 hydrogen -- a partial pressure -- : -- 140 -- [-- atm --] -- H -- two -- /-- Oil -- : -- 1000 -- [-- Nm --
 three -- /-- kl --] -- temperature -- : -- 375 -- degree C -- LHSV -- : -- 0.2 -- [-- one -- /-- hr --] --
 obtaining -- having had -- DAO -- and -- refined oil -- six -- stock oil -- receiving -- a yield -- a
 20 hydrogen content -- each -- a process -- it can set -- a hydrogen content -- augend -- V+nickel -- a
 content -- CCR -- sulfur -- concentration -- Table 4 -- be shown .

[0055]

[Table 4]

| | 原料油 | 実施例5 | | 実施例6 | |
|-----------------|-------|-------|-------|-------|-------|
| | | DAO | 精製油5 | DAO | 精製油6 |
| 得率 (wt %) | 100 | 63 | 59 | 65 | 59 |
| 水素含有量 (wt %) | 10.68 | 11.83 | 12.71 | 11.68 | 12.96 |
| 水素含有量増加量 (wt %) | — | 1.15 | 0.88 | 1.00 | 1.28 |
| 合計水素増加量 (wt %) | — | — | 2.03 | — | 2.28 |
| V+Ni (wt ppm) | 246.0 | 41.0 | <0.1 | 45.0 | <0.1 |
| コナソリ残留炭素 (wt %) | 25.00 | 11.60 | 0.56 | 11.90 | 0.36 |
| S (wt %) | 5.50 | 4.30 | 0.20 | 4.32 | 0.13 |

[0056] After carrying out extraction separation and obtaining DAO using the same stock oil as
 example of comparison 6 example 5 so that it may become extractability (solvent/Oil ratio: 8/1)
 65wt% using an isobutane solvent, purification processing of the DAO was carried out on the
 30 following hydrorefining conditions, and comparative refined oil F was obtained.
 hydrorefining -- conditions -- : -- nickel/Mo+Co/Mo -- a catalyst (it is 2/8 at a volume ratio) --
 hydrogen -- a partial pressure -- : -- 80 -- [-- atm --] -- H -- two -- /-- Oil -- : -- 800 -- [-- Nm --
 three -- /-- kl --] -- temperature -- : -- 340 -- degree C -- LHSV -- : -- 0.5 -- [-- one -- /-- hr --] --
 obtaining -- having had -- DAO -- and -- refined oil -- F -- stock oil -- receiving -- a yield -- a
 35 hydrogen content -- each -- a process -- it can set -- a hydrogen content -- augend -- V+nickel -- a
 content -- CCR -- sulfur -- concentration -- Table 5 -- be shown .

[0057] Using the same stock oil as example of comparison 7 example 5, extraction separation
 was carried out and comparative refined oil G was obtained so that it might become
 40 extractability (solvent/Oil ratio: 8/1) 55wt% using an isobutane solvent. The augend of the yield
 to the stock oil of the obtained refined oil G, a hydrogen content, and the hydrogen content in
 each process, a V+nickel content, CCR, and sulfur concentration are shown in Table 5.

5 [0058] Using the same stock oil as example of comparison 8 example 5, purification processing was carried out on the following hydrorefining conditions, and comparative refined oil H was obtained.

hydrorefining -- conditions -- : -- nickel/Mo+Co/Mo -- a catalyst (it is 3/7 at a volume ratio) -- hydrogen -- a partial pressure -- : -- 140 -- [-- atm --] -- H -- two -- / -- Oil -- : -- 1000 -- [-- Nm -- three -- / -- kl --] -- temperature -- : -- 375 -- degree C -- LHSV -- : -- 0.2 -- [-- one -- / -- hr --] -- obtaining -- having had -- refined oil -- H -- stock oil -- receiving -- a yield -- a hydrogen content -- each -- a process -- it can set -- a hydrogen content -- augend -- V+nickel -- a content -- CCR -- sulfur -- concentration -- Table 5 -- be shown -- .

15 [0059]
[Table 5]

| | 原料油 | 比較6 | | 比較7 | 比較8 |
|-----------------|-------|-------|-------|----------|-----------|
| | | DAO | 精製油F | G (抽出のみ) | H (水素化のみ) |
| 得率 (wt %) | 100 | 65 | 61 | 55 | 91 |
| 水素含有量 (wt %) | 10.68 | 11.68 | 12.08 | 11.88 | 11.69 |
| 水素含有量増加量 (wt %) | — | 1.00 | 0.40 | 1.20 | 1.01 |
| 合計水素増加量 (wt %) | — | — | 1.40 | 1.20 | 1.01 |
| V+Ni (wt ppm) | 246.0 | 45.0 | <0.1 | 26.0 | 32.0 |
| コークス残留炭素 (wt %) | 25.00 | 12.20 | 3.91 | 9.20 | 9.25 |
| S (wt %) | 5.50 | 4.32 | 2.60 | 4.09 | 1.31 |

20 [0060] Using respectively the last refined oil obtained in the example examples 5-6 of low-grade olefin manufacture, and the examples 6-8 of a comparison, it pyrolyzes on the same conditions as the above, and the yield of the obtained low-grade olefin, the yield of byproduction heavy oil, and the decision result of continuous-running nature are shown in Table 6.

25 [0061]
[Table 6]

| | 実施例5 | 実施例6 | 比較6 | 比較7 | 比較8 |
|----------------|-------|-------|-------|-------|-------|
| 水素含有量 (wt %) | 12.71 | 12.96 | 12.08 | 11.88 | 11.69 |
| エチレン収率 (wt %) | 18.1 | 19.1 | 13.5 | 13.1 | 12.1 |
| プロピレン収率 (wt %) | 14.7 | 15.2 | 9.4 | 9.1 | 8.6 |
| 副生重質油 (wt %) | 25.0 | 23.8 | 33.2 | 35.9 | 36.1 |
| 連続運転性 | ○ | ○ | × | × | × |

30 [0062] the examples 5-6 of this invention -- solvent extraction down stream processing -- setting -- heavy stock oil -- comparing -- a hydrogen content -- more than 0.2wt% -- hydrorefining down stream processing which extracts so that it may increase, and continues -- setting -- DAO -- comparing -- a hydrogen content -- more than 0.5wt% -- it increases -- as -- processing -- **** -- as a result -- the last refined oil -- stock oil -- receiving -- more than 0.7wt% -- it is increasing. In the refined oil of obtained this invention, as for 0.1 or less wtppms and CCR, the nickel+V concentration of less than [1wt%] and sulfur concentration is less than [0.5wt%], and the refined oil of the high quality from which the impurity was removed by altitude is obtained by each.

[0063] On the other hand, in the comparison 7 refined only by solvent extraction processing, recovery is made low even to 55% and it turns out that removal of an impurity is not enough even if it carries out extract purification. moreover, although hydrotreating is the same conditions when the example 6 of this invention is compared with the comparison 8 refined only by hydrotreating, after it turning out that a big difference is in removal of an impurity and increasing a predetermined hydrogen content by solvent extraction processing beforehand, by carrying out hydrotreating processing shows that it is markedly alike, an impurity is removed and the refined oil of high quality is obtained. Furthermore, by the result of having carried out pyrolysis processing of the obtained refined oil, and having manufactured the low-grade olefin, by the refined oil of this invention, ethylene yield exceeded 15%, propylene yield is over 10% and continuous-running nature was further judged to be the possible range from the generation situation of byproduction heavy oil. On the other hand, in the example of a comparison with which are not satisfied of this invention, ethylene yield does not exceed 15%, but further, there are many amounts of generation of byproduction heavy oil, and it turns out that each continuous-running nature has a problem.

[0064] Distillation separated into the distillate and the residue oil the ARABIAN heavy crude oil of manufacture API gravity 27.4 of the refined oil which used example 10 heavy crude as the start base, hydrotreating of a part of distillate was carried out, and GO was obtained. On the other hand, solvent extraction processing and hydrotreating processing were carried out on the same conditions as the example 1 of this invention by having made into stock oil 1 the heavy oil of API gravity 10.9 which is a residue oil, and refined oil 10 was obtained. A part of stock oil 2 (they are 10 weight sections to the crude oil 100 weight section) was mixed, a part of this refined oil 10 (they are 20 weight sections to the crude oil 100 weight section) and Above GO were used as a pyrolysis raw material for low-grade olefin manufacture, and the low-grade olefin was manufactured. The yield of the ordinary pressure residual oil of an example 10, a deasphaltene oil, a hydrotreating deasphaltene oil, and a heavy ethylene raw material, a hydrogen content, a nickel+V metal content, a CCR content, and S content are shown in Table 7.

[0065]

[Table 7]

| | 原料油 1 | | | 原料油 2 | 原料油 (1+2) |
|--------------------|-------|-------|-------|-------|----------------------|
| | 常圧残油 | DAO | 精製油10 | GO | 精製油 10 : 20, GO : 10 |
| 得率 (wt %) (原油=100) | 61 | 49 | 45 | 18 | 30 |
| 水素含有量 (wt %) | 11.20 | 11.42 | 11.95 | 13.70 | 12.53 |
| 水素含有量増加量 (wt %) | — | 0.22 | 0.53 | — | — |
| 合計水素増加量 (wt %) | — | — | 0.75 | — | — |
| V+Ni (wt ppm) | 153.0 | 14.2 | 0.7 | <0.1 | <0.1 |
| コファクタ残留炭素 (wt %) | 12.50 | 3.60 | 1.90 | 0.00 | 1.20 |
| S (wt %) | 4.70 | 3.50 | 0.40 | 0.05 | 0.27 |
| エチレン収率 (wt %) | — | — | — | — | 17.6 |
| プロピレン収率 (wt %) | — | — | — | — | 14.1 |
| 副生重質油 (wt %) | — | — | — | — | 25.8 |
| 連続運転性 | — | — | — | — | ○ |

[0066] It has checked that it was the result of mixing a distillate with the low high impurity concentration separately prepared to the refined oil obtained by performing purification processing of this invention by making a residue oil into stock oil, considering as the raw

5 material for low-grade olefin manufacture, and being able to be satisfied with an example 10 of both the yield of ethylene and a propylene, and continuous-running nature.

[0067]

10 [Effect of the Invention] If the purification approach of this invention is used, a hydrogen content becomes possible [obtaining the refined oil which refined certainly and economically the heavy oil not more than 12wt% and reduced the impurity], it is limited conventionally, and the application of heavy oil can make it expand sharply. Moreover, when the refined oil obtained by this approach is used as a raw material for low-grade olefin manufacture, ethylene and a propylene can be manufactured with the yield which balances economically, and it can consider
15 as the range in which commercial operation is possible also about continuous-running nature further.

20 TECHNICAL FIELD

[Field of the Invention] This invention relates to the purification approach of heavy oil that the refined oil also suitable for the raw material for low-grade olefin manufacture can be obtained from the heavy oil which was not used for the raw material for low-grade olefin manufacture,
25 conventionally especially about the purification approach of the heavy oil by solvent extraction processing and hydrotreating processing in which the impurity of the crude oil origin is efficiently removable.

30 EFFECT OF THE INVENTION

[Effect of the Invention] If the purification approach of this invention is used, a hydrogen content becomes possible [obtaining the refined oil which refined certainly and economically the heavy
35 oil not more than 12wt% and reduced the impurity], it is limited conventionally, and the application of heavy oil can make it expand sharply. Moreover, when the refined oil obtained by this approach is used as a raw material for low-grade olefin manufacture, ethylene and a propylene can be manufactured with the yield which balances economically, and it can consider
40 as the range in which commercial operation is possible also about continuous-running nature further.

TECHNICAL PROBLEM

45 [Description of the Prior Art] Since the impurity originating in the origin exists in a crude oil, the petroleum product which uses a crude oil as starting material performs various kinds of physical or chemical purification processings including ordinary pressure and vacuum distillation separation, and is produced. Generally a petroleum fraction, i.e., the distillate separated from the
50 overhead by distillation, has few above-mentioned impurities, and it is used from an impurity

5 being removable by easy purification processing as high-class fuel oil, the raw materials for petrochemistry, etc., such as motor fuel which is the petroleum product of high quality from which the impurity was removed highly, and a gas turbine fuel.

10 [0003] On the other hand, about heavy oil, such as gas oil, an impurity is condensed, the amount exists with the gestalt which many [not only], but is very hard to be removed, and a limitation is in the impurity removal by hydrotreating which is a fundamental purification means. When refining especially to altitude, the severe reaction condition of an elevated temperature and high pressure is required under existence of hydrogen and a catalyst, and a lot of hydrogen and catalysts are consumed, and a large amount of investment also including an installation cost is
15 needed, and the present condition is that is not economical. Therefore, from heavy oil, added value is high, namely, it looks forward to the method of obtaining that it is simple and economically the quality refined oil from which the impurity was removed by altitude.

20 [0004] Quality refined oil has the use as a raw material for petrochemistry as one of the application of the. Although *****, such as ethane and naphtha, are manufactured by the pyrolysis as raw materials with main low-grade olefins which are the basic matter of a petrochemical field, such as ethylene and a propylene, the fraction with heavy light gas oil, vacuum gas oil, etc. is also partly used also as a raw material. Although the ethylene plant which used the former ethane as the raw material is in use in the U.S. and the Middle East where
25 natural gas is abundant and cheap, in Japan where naphtha is cheaper, Asia, and Europe, it is using the latter naphtha as a raw material in most cases.

30 [0005] Since it increases more than the case where generation of by-products, such as tar and a pitch, uses ethane as a raw material, caulking by pyrolysis tubing which is a main reaction machine, and the quenching heat exchanger of the latter part, and the correspondence to fouling are needed in the ethylene plant which used naphtha as the raw material. And molecular weight is larger than naphtha and the vacuum gas oil with many metals and sulfur contents is considered to be the limitation in which commercial operation is possible as a raw material of an ethylene
35 plant.

[0006] On the other hand, if stock oil heavier than a gas oil fraction can be used as a raw material for low-grade olefin manufacture from a viewpoint of the amount of feeding, and raw material cost, while raw material cost is cheap, the problem on adequate supply of the stock oil accompanying heavy-izing of petroleum resources can also be solved, and it will become a very
40 big contribution on industry.

[0007] It is what offers the approach of collecting the high refined oil of added value from the heavy oil which it succeeds in this invention in view of the above-mentioned situation, and contains the impurity of the crude oil origin by high concentration economically. By carrying out
45 purification processing of the heavy oil, such as ordinary pressure residue made conventionally unsuitable especially as a raw material for low-grade olefins, by the easy and positive approach, it is offering the purification approach of heavy oil the refined oil which was economically suitable also for the raw material for low-grade olefin manufacture being recoverable.

50

MEANS

10 [Means for Solving the Problem] As a result of inquiring wholeheartedly that this invention
persons should attain the above-mentioned purpose, a hydrogen content uses the heavy oil not
more than 12wt% as a raw material. By processing the deasphaltene oil which processed so that
a hydrogen content might be increased more than a constant rate by solvent extraction, then was
obtained so that a hydrogen content may be increased more than a constant rate by hydrorefining
processing The impurity in heavy oil could remove efficiently and a header and this invention
15 were completed for the refined oil of the high quality from which the impurity was removed by
altitude being obtained.

[0009] Namely, the solvent extraction process which this invention carries out solvent extraction
processing of the stock oil, and obtains extracted oil, It is the purification approach of heavy oil
20 of obtaining refined oil by processing including the hydrorefining process which carries out the
hydrogen treating of the obtained extracted oil to the bottom of existence of hydrogen and a
catalyst, and obtains refined oil. Stock oil A hydrogen content is heavy oil not more than 12wt%,
and the stock oil is introduced into a solvent extraction process. a hydrogen content -- stock oil --
receiving -- more than 0.2wt% -- with the solvent extraction process which carries out solvent
25 extraction processing and obtains the deasphaltene oil (DAO) which is extracted oil so that it
may increase a deasphaltene oil -- a hydrorefining process -- introducing -- a hydrogen content --
a deasphaltene oil -- receiving -- more than 0.5wt% -- the purification approach of the heavy oil
characterized by having the hydrorefining process which carries out hydrorefining and obtains
refined oil so that it may increase is offered.

30 [0010] Since the impurity which is hard to be removed by latter hydrorefining by taking this
configuration is processed on the conditions which a hydrogen content increases more than a
constant rate by solvent extraction beforehand and it processes on the conditions which a
hydrogen content increases more than a constant rate according to a hydrorefining process after
35 that, in each purification process independent, the refined oil of the high quality from which the
impurity was removed by inestimable altitude can be obtained certainly. this invention person
etc. only by carrying out a solvent extraction process and hydrorefining processing simply By
processing by making into an index the hydrogen content of the heavy oil which processes an
impurity paying attention to the ability not to carry out certainly, so that the hydrogen content of
40 the specified quantity may be made to increase at a solvent extraction process and the
hydrorefining process following it, respectively It can obtain on the economical conditions at
which it finds out that the refined oil from which the impurity was removed by altitude can be
obtained, the conditions of a solvent extraction process and a hydrorefining process are not made
into a severe condition certainly and efficiently, and the balance of a load is maintained.

45 [0011] Furthermore, the hydrogen content of the refined oil obtained above in this invention
offers the purification approach of more than 11.5wt% and the heavy oil with which it is
characterized by being more than 12.0wt% preferably. When the refined oil obtained by this is
applied to the raw material for low-grade olefin manufacture which is a raw material for
50 petrochemistry, caulking and generating of fouling are suppressed also in the case of a pyrolysis

5 reaction, and the commercial operation of it becomes possible. The purification approach of this reason to this invention is the approach of having been economically excellent which can obtain the high refined oil of added value certainly and efficiently.

[0012]

10 [Embodiment of the Invention] A hydrogen content processes [by using 10 - 12wt% heavy oil as a raw material] this invention preferably, respectively on less than [12wt%] and the conditions which attain whenever [predetermined purification] in a solvent extraction process and hydrotreating down stream processing, respectively. Generally residue oils, such as ordinary pressure residual oil, super-heavy crude, etc. corresponded, and since high impurity
15 concentration was high, as for the heavy oil not more than 12wt% used for this invention, the application was limited. The hydrogen content of these heavy oil is 9 - 12.5 % of the weight, many are 9 - 11.5 % of the weight, and generally, even if refined conventionally, it was fully unremovable, and it was not used for the raw materials for petrochemistry for low-grade olefins etc., the impurity having been used as unsuitable.

20 [0013] this invention -- a hydrogen content -- the heavy oil not more than 12wt% -- stock oil -- carrying out -- as the 1st process -- solvent extraction processing -- carrying out -- a hydrogen content -- more than 0.2wt% -- the deasphaltene oils which are the extracted oil which increased are collected. In this solvent extraction down stream processing, a part for an asphaltene with
25 few hydrogen contents is removed alternatively. The amount of this asphaltene is having micellar structure which hydrogen contents, such as condensed multi-ring aromatic series and a cycloparaffin ring, become from few compounds, the porphyrin compound of metals, such as carbon residue, and V, nickel, contains it in that interior, and it is known that the impurity is condensed. and the amount of asphaltene controls a hydrotreating reaction remarkably, and it
30 also knows promoting degradation of a catalyst -- having -- **** -- this invention -- setting -- a hydrogen content -- more than 0.2wt% -- as a result, the specified quantity of an asphaltene is alternatively removed by carrying out solvent extraction processing on the increasing conditions.

[0014] Solvent extraction processing can apply solvent deasphalting processing in which it is
35 known conventionally, and divides it into a deasphaltene oil and the asphaltene by which there are few hydrogen contents and metal and carbon residue are condensed by carrying out counterflow contact of the heavy oil with the solvent of C3-C5 in a solvent extraction column. and the thing for which the amount of solvents to the class and heavy oil of a solvent to be used and extract temperature conditions are chosen suitably -- a hydrogen content -- more than
40 0.2wt% -- extract processing conditions can be controlled and the extracted oil of this invention can be obtained so that it may increase. As a solvent of C3-C5, as being chosen out of a propane, butane, and a pentane, one is preferably used as it is few.

[0015] Deasphaltene oils can be collected from the overhead section of an extraction column as
45 an extract with a solvent, and the solvent in an extract can be obtained by carrying out separation removal in the state of supercritical. About an asphaltene, these is collected from the bottom section as raffinate with some solvents, and the solvents in raffinate are collected by evaporation.

[0016] the hydrogen content of the deasphaltene oil obtained by this solvent extraction down
50 stream processing in this invention -- the hydrogen content of raw material heavy oil -- more

5 than 0.2wt% -- it is increasing. furthermore, 0.2 - 1.5wt% -- increasing -- desirable -- 0.2 - 1.2wt% -- especially the thing to increase is desirable.

10 [0017] Furthermore, it is desirable to change the augend of the hydrogen content of solvent extraction processing with the value of the hydrogen content of raw material heavy oil. That is, when the hydrogen content of stock oil is more than 11wt%, in a solvent extraction process, it is desirable to control extract processing conditions to stock oil to become 0.2 - 0.5wt% of increment in a hydrogen content especially 0.2 - 1.0wt%. Moreover, if a hydrogen content is less than [11.0wt%], the augend of the range of 0.5 - 1.5wt%, especially 0.8 - 1.3wt% is desirable.

15 [0018] Since removal of an impurity fully becomes impossible even if it becomes inadequate removing [of the asphaltene which is an impurity as it is less than / 0.2wt%] the increment in the hydrogen content in a solvent extraction process and it processes it at a latter hydrorefining process, they are indispensable conditions. although it is better on the other hand as the upper limit of the augend is large from a viewpoint of whenever [purification] -- more than 1.5wt% --
20 since the recovery of a deasphaltene oil falls in making it increase, it is not economical.

[0019] this invention -- the above-mentioned solvent extraction processing -- a hydrogen content -- more than 0.2wt% -- hydrorefining processing of the deasphaltene oil which carried out solvent extraction processing so that it might increase is carried out as the 2nd continuing
25 process. hydrorefining processing of this invention -- setting -- a hydrogen content -- more than 0.5wt% -- it processes on the increasing conditions. This hydrorefining processing is typical purification processing which processes a hydrocarbon with elevated-temperature high pressure under existence of a catalyst and hydrogen, and can include all the reactions, such as hydrocracking, hydrodesulfurization, hydrogenation demetallization, and hydrogenation
30 denitrification. Namely, the sulfur compound in hydrocracking which obtains low-molecular-weight refined oil from raw material heavy oil, and a hydrocarbon is made to react with hydrogen. Hydrodesulfurization which dissociates by making it a hydrogen sulfide and obtains the refined oil of low-sulfur concentration from stock oil, Hydrogenate the metallic compounds which are in a hydrocarbon under elevated-temperature high-pressure hydrogen, make it an
35 element-like metal, and deposition is carried out on a catalyst. The nitride in a hydrocarbon may be made to react with hydrogen under the hydrogenation demetallization which obtains the refined oil of low metal concentration, and elevated-temperature high-pressure hydrogen, and you may dissociate by making it ammonia, and may also include all the reactions, such as hydrogenation denitrification which obtains the refined oil of low nitrogen concentration from
40 stock oil.

[0020] Although a sulfur content, a metal, etc. are contained in heavy oil as an impurity, since removing only at a hydrorefining process beforehand by solvent extraction down stream processing of the preceding paragraph has removed the difficult impurity, an impurity can be
45 efficiently removed to low concentration, without making it a severe condition. It is desirable to use as a catalyst used for hydrorefining processing of this invention combining at least two kinds chosen from a hydrogenation demetallization catalyst, a hydrodesulfurization catalyst, a hydrodesulfurization demetallization catalyst, and a hydrocracking catalyst. It is the Co/Mo, nickel/Co/Mo, and nickel/Mo system preferably as a catalyst used for hydrorefining.
50

5 [0021] Although there is especially no limit in the conditions of a hydrotreating reaction, the
range of the hydrotreating reaction condition currently generally performed is desirable. That is,
a hydrogen partial pressure has desirable 60-150kg/cm², and especially its 80-130kg/cm² is
desirable. Moreover, hydrogen / oil ratio has desirable 400-1200Nm³/kl, and especially its 600-
1000Nm³/kl is desirable. 1.0 [0.1-]/hr of LHSV is desirable, and 0.8 [0.2-]/especially its hr is
10 desirable. 340-440 degrees C of reaction temperature are desirable, and especially its 350-420
degrees C are desirable.

[0022] these conditions -- the general conditions of hydrotreating -- it is -- this invention --
setting -- after the solvent extraction process of the preceding paragraph -- a hydrogen content --
15 more than 0.5wt% -- if a hydrotreating process is performed on the increasing conditions, the
impurity as the last refined oil is efficiently removable. In this invention, when the hydrogen
content of stock oil is 11 - 12wt%, as for the increment in the hydrogen content to the
deasphaltene oil of the refined oil obtained at a hydrotreating process, it is especially desirable
that it is 0.5 - 0.9wt% 0.5 - 1.0wt%. Moreover, when the hydrogen content of stock oil is less
20 than [11wt%], as for the increment in the hydrogen content to the deasphaltene oil of the
refined oil obtained at a hydrotreating process, it is especially desirable that it is 0.8 - 1.3wt% 0.6
- 1.5wt%.

[0023] Furthermore, it is desirable that it is 0.5 - 1.0wt% augend if the hydrogen content of the
25 deasphaltene oil obtained at the solvent extraction process of the preceding paragraph is more
than 11.5wt%, and if the augend of the hydrogen content in hydrotreating down stream
processing of this invention is less than [11.5wt%], it is desirable [augend] that it is 0.6 -
1.5wt% augend. When impurity removal of a deasphaltene oil becomes it inadequate that the
augend of a hydrogen content is less than [0.5wt%] in hydrotreating down stream processing
30 and it makes it the augend beyond 1.5wt%, it is not economical in order to have to make severe
the processing conditions of hydrotreating reactions, such as a hydrogen partial pressure,
reaction temperature, and a catalyst fill.

[0024] That is, without making a hydrogen partial pressure and reaction temperature extremely
35 high in hydrotreating down stream processing which continues by removing beforehand
alternatively a part for the asphaltene which is the impurity which is hard to be removed by
hydrotreating down stream processing in solvent extraction down stream processing, if it states
from a viewpoint of the reaction condition of hydrotreating, even if it makes the amount of
catalysts increase sharply and does not lengthen reaction time, an impurity can be efficiently
40 removed to low concentration. Consequently, parts for a metal, such as KONRADSON carbon
residue, nickel, V, etc. which exist with the gestalt which condenses and is hard to be removed in
an asphaltene, are alternatively removed by solvent extraction, and, subsequently can remove
intensively impurities, such as metals, such as the sulfur and nickel which exist with the gestalt
which is easy to be removed, and V, by hydrotreating processing.

45 [0025] When applying the refined oil processed at the purification process by above-mentioned
this invention to the raw material for low-grade olefin manufacture and carrying out elevated-
temperature pyrolysis, since the impurity used as the causative agent of caulking or fouling is
reduced certainly and efficiently, it can be applied to commercial production from the yield and
50 continuous-running nature of a low-grade olefin. This means that quality refined oil can be

5 obtained for the heavy oil considered to be conventionally unsuitable as a low-grade olefin raw material, such as a residue oil and super-heavy crude, by purification simple as starting material.

10 [0026] Moreover, in this invention, if it is the refined oil processed on the conditions with which are satisfied of the above, it is effective as refined oil of this invention, but when using as a raw material for low-grade olefin manufacture especially, it is required for a hydrogen content to be more than 11.5wt%, and it is more desirable that it is more than 12.0wt%.

15 [0027] In this invention, it is required for the hydrogen content of the refined oil obtained by solvent extraction and two steps of purification of hydrorefining to increase heavy oil from raw material heavy oil by 0.7% of the weight or more, it is desirable that it is 0.8 - 2.7wt%, and it is desirable that it is further 1.0 - 2.2wt%. Moreover, when using as a raw material for low-grade olefin manufacture, as for the hydrogen content of the last refined oil, it is desirable that it is more than 11.5wt%, and it is still more desirable that it is 12.0 - 13.5wt%.

20 [0028] the hydrogen content of refined oil -- more than 11.5wt% and raw material heavy oil -- more than 0.7wt% -- by performing solvent extraction processing and hydrorefining processing so that it may increase The property in each processing is complemented mutually and does not cover an excessive load over the equipment for the solvent extraction of each process, and hydrorefining. The refined oil refined by altitude can be obtained by high yield, and when it
25 applies to the raw material for petrochemistry, the refined oil which it was hard coming to generate caulking and fouling, and was suitable for the raw material for petrochemistry by high yield can be manufactured.

30 [0029] the process which carries out solvent extraction processing of the heavy oil of this invention -- setting -- the hydrogen content of the stock oil -- more than 0.2wt% -- although extract operation is carried out on the increasing conditions -- a nickel+V metal -- the inside of a residue oil and super-heavy crude -- several -- it is contained 10-thousands wtpm(s). Since these are condensed by the asphaltene, and exist and an asphaltene can be alternatively removed at a solvent extraction process, it is desirable to set especially to 50 or less wtpms 70 or less wtpms
35 of metal concentration of nickel+V in the deasphaltene oil which is extract refined oil about the content in a deasphaltene oil by solvent extraction processing. Moreover, it is desirable less than [15wt%] and that a carbon residue content performs solvent extraction processing so that it may become less than [12wt%] especially. namely, solvent extraction processing -- a hydrogen content -- 0.2wt(s)% -- while making it increase, it is desirable to make nickel+V metal
40 concentration to 70 or less wtpms, and to make KONRADSON carbon residue into less than [15wt%], without making the conditions of latter hydrorefining processing severe by this, an impurity can be removed certainly and the refined oil of high quality can be obtained.

45 [0030] Moreover, it is desirable less than [5wt%] and to make sulfur concentration of a deasphaltene oil into less than [4wt%] especially. the sulfur content of the last refined oil obtained by that cause by the continuing hydrorefining processing -- less than [0.5wt%] -- it can process certainly so that it may become less than [0.3wt%] preferably. the nickel+V concentration of the last refined oil from which 70 or less wtpms and carbon residue concentration are obtained in the nickel+V concentration of a deasphaltene oil by the
50 hydrorefining processing which continues when less than [15wt%] and sulfur concentration

5 consider as less than [5wt%] -- 2 or less wtppps -- desirable -- 1 or less wtpm and carbon
residue concentration -- less than [1wt%] and sulfur concentration -- less than [0.5wt%] -- it
can process certainly so that it may become less than [0.3wt%] preferably. By making the sulfur
content of the last refined oil into 0.5 or less % of the weight, when it uses as stock oil for low-
10 grade olefins, the corrosion of pyrolysis equipment can be suppressed in the tolerance of an
ingredient, and commercial manufacture of the substantial raw material for low-grade olefins can
be enabled.

[0031] Especially in this invention, it is desirable to perform solvent extraction processing and
hydrorefining processing so that 2 or less wtppps of nickel+V metal contents of the last refined
15 oil may be set to 1.0 or less wtppps. By setting a nickel+V metal content to 1 or less wtpm for
the deasphaltene oil with which the nickel+V metal content turned into below the 70 weight ppm
by solvent extraction processing further by hydrorefining, it can reduce caulking remarkably,
refined oil can be obtained by high yield, and the refined oil can be used as a pyrolysis raw
material for low-grade olefin manufacture.

20 [0032] In the industrial method of manufacturing the low-grade olefin containing ethylene and a
propylene by the pyrolysis reaction, the maintenance nature to fouling and olefin yield by
decoking or byproduction heavy oil influence the economical efficiency, and 25% or more of
especially yield of a low-grade olefin serves as a standard. If a low-grade olefin is furthermore
25 seen in detail, 10% or more of propylene yield will become [ethylene yield] a standard 15% or
more.

[0033] Moreover, about fouling by caulking and byproduction heavy oil which influence the
maintenance nature of pyrolysis equipment, it corresponds in periodical decoking and cleaning.
30 In order to prevent too much decomposition, in case it quenches especially the hot
decomposition product disassembled with decomposition tubing about byproduction heavy oil by
down-stream heat exchange, when there are many amounts of generation of heavy oil, it
blockades a heat exchanger and piping, and makes long-term continuous running impossible.
When leaving heavy oil like this invention, the amount of generation of the byproduction heavy
35 oil in a pyrolysis reaction can consider as the standard of commercial operation.

[0034] When the hydrogen content with which the refined oil obtained by this invention is not
conventionally used for raw materials for low-grade olefin manufacture, such as ethylene, carries
out purification processing and offers the heavy oil not more than 12wt% as a raw material for
40 low-grade olefin manufacture, the olefin yield and the caulking property at the time of a
pyrolysis are good, and make industrial production possible.

[0035] When there are few contents of the impurity in the distillate obtained in mere distillation
separation of a crude oil etc. in this invention, or when the content of an impurity can be reduced
45 by easy purification By using a crude oil as a start raw material, it separates into a distillate and a
residue oil, and at least solvent extraction and the part which carried out hydrorefining
processing, considered as refined oil, and carried out hydrorefining of the above-mentioned
distillate to this refined oil can be mixed as mentioned above, and the atmospheric-distillation
residue oil and vacuum-distillation-residue oil which are a residue oil can also be made into

5 refined oil.

10 [0036] In this case, if a solvent extraction process and a hydrorefining process satisfy the increment criteria of the hydrogen content of this invention, by mixing a distillate with few impurity contents, the whole high impurity concentration can be decreased, the amount of supply of refined oil can be made to increase further, and it will become things. When supplying as stock oil for low-grade olefin manufacture, it is further hard coming to generate caulking and fouling in a pyrolysis reaction, and they can enable commercial production.

15 EXAMPLE

[Example] Next, although an example is shown and this invention is further explained to a detail, this invention is not limited to the following examples.

20 [0038] the heavy oil (hydrogen content: -- 11.25 [wt%] --) examples 1-4 and the example 1 of a comparison - whose 5 example 1 API gravity are the residue oils of 14.3 nickel+V metal: -- 65 [wtppm] and KONRADSON carbon residue (it is called Following CCR): -- 11.1 [wt%] -- It introduces into a solvent extraction processor by making S:3.95 [wt%] into stock oil. After carrying out extraction separation and obtaining a deasphaltene oil (it is called the following DA 0) so that it may become extractability (solvent/Oil ratio: 8/1) 81wt% using a normal pentane solvent, purification processing of the deasphaltene oil was carried out on the following hydrorefining conditions, and the refined oil 1 of this invention was obtained.

25 hydrorefining condition: -- nickel/Mo+nickel/Co/Mo catalyst (it is 1/9 at volume ratio), and hydrogen partial pressure:90[atm] H₂ / Oil ratio: -- 600 [Nm³/kl] and temperature: -- 380 degrees C of the augend of the yield to the stock oil of the deasphaltene oil LHSV:0.5 [1/hr] obtained and refined oil 1, a hydrogen content, and the hydrogen content in each process, V+nickel contents, CCR(s), and sulfur concentration are shown in Table 1. The hydrogen content was measured by the CHN elemental-analysis method.

35 [0039] The stock oil used in the example 2 example 1 was introduced into the solvent extraction processor, after carrying out extraction separation and obtaining a deasphaltene oil so that it may become extractability (solvent/Oil ratio: 8/1) 84wt% using a normal pentane solvent, hydrorefining of the DAO was carried out on the same conditions as an example 1, and the refined oil 2 of this invention was obtained. The augend of obtained DAO and the yield to the stock oil of refined oil 2, a hydrogen content, and the hydrogen content in each process, a V+nickel content, CCR, and sulfur concentration are shown in Table 1.

45 [0040] The stock oil used in the example 3 example 1 was introduced into the solvent extraction processor, after carrying out extraction separation and obtaining DAO so that it may become extractability (solvent/Oil ratio: 8/1) 81wt% using a normal pentane solvent, purification processing of the DAO was carried out on the following hydrorefining conditions, and the refined oil 3 of this invention was obtained.

50 hydrorefining condition: -- nickel/Mo+nickel/Co/Mo catalyst (it is 1/9 at volume ratio), and hydrogen partial pressure:85[atm] H₂ / Oil ratio: -- 600 [Nm³/kl] and temperature: -- 360

5 degrees C of the augend of DAO LHSV:0.5 [1/hr] obtained and the yield to the stock oil of refined oil 3, a hydrogen content, and the hydrogen content in each process, V+nickel contents, CCR(s), and sulfur concentration are shown in Table 1.

10 [0041] The stock oil used in the example 4 example 1 was introduced into the solvent extraction processor, after carrying out extraction separation and obtaining DAO so that it may become extractability (solvent/Oil ratio: 8/1) 76wt% using an isobutane / normal pentane mixed solvent, purification processing of the DAO was carried out on the following hydrotreating conditions, and the refined oil 4 of this invention was obtained.

15 hydrotreating condition: -- nickel/Mo+nickel/Co/Mo catalyst (it is 1/9 at volume ratio), and hydrogen partial pressure:110[atm] H₂ / Oil ratio: -- 800 [Nm³/kl] and temperature: -- 380 degrees C of the augend of DAO LHSV:0.3 [1/hr] obtained and the yield to the stock oil of refined oil 3, a hydrogen content, and the hydrogen content in each process, V+nickel contents, CCR(s), and sulfur concentration are shown in Table 1.

20 [0042]

[Table 1]

| | 原料油 | 実施例 1 | | 実施例 2 | | 実施例 3 | | 実施例 4 | |
|------------------|-------|-----------|-------|-----------|-------|-----------|-------|-----------|-------|
| | | DAO 精製油 1 | | DAO 精製油 2 | | DAO 精製油 3 | | DAO 精製油 4 | |
| 得率 (wt %) | 100 | 81 | 77 | 84 | 79 | 81 | 78 | 76 | 72 |
| 水素含有量 (wt %) | 11.25 | 11.55 | 12.33 | 11.50 | 12.28 | 11.55 | 12.14 | 11.75 | 12.65 |
| 水素含有量増加量 (wt %) | — | 0.30 | 0.78 | 0.25 | 0.78 | 0.30 | 0.59 | 0.50 | 0.90 |
| 合計水素増加量 (wt %) | — | — | 1.08 | — | 1.03 | — | 0.89 | — | 1.40 |
| V+Ni (wt ppm) | 65.0 | 7.3 | <0.1 | 10.7 | <0.1 | 7.3 | <0.1 | 3.7 | <0.1 |
| ジソド*の残留炭素 (wt %) | 11.10 | 2.60 | 0.41 | 3.20 | 0.62 | 2.60 | 0.76 | 1.80 | 0.21 |
| S (wt %) | 3.95 | 3.35 | 0.06 | 3.45 | 0.16 | 3.35 | 0.26 | 3.19 | 0.02 |

25 [0043] Except having made the rate of solvent extraction into 88% using the same stock oil as example of comparison 1 example 1, after carrying out extraction separation by the same extraction condition as an example 1 and obtaining DAO, hydrotreating of the DAO was carried out on the following hydrotreating conditions, and comparative refined oil A was obtained.

30 hydrotreating -- conditions -- : -- nickel/Mo+Co/Mo -- a catalyst (it is 1/9 at a volume ratio) -- hydrogen -- a partial pressure -- : -- 90 -- [-- atm --] -- H -- two -- /-- Oil -- : -- 600 -- [-- Nm -- three -- /-- kl --] -- temperature -- : -- 360 -- degree C -- LHSV -- : -- 0.5 -- [-- one -- /-- hr --] -- obtaining -- having had -- DAO -- and -- refined oil -- A -- stock oil -- receiving -- a yield -- a hydrogen content -- each -- a process -- it can set -- a hydrogen content -- augend -- V+nickel -- a content -- CCR -- sulfur -- concentration -- Table 2 -- be shown .

35 [0044] After carrying out extraction separation and obtaining DAO using the same stock oil as example of comparison 2 example 1 so that it may become extractability (solvent/Oil ratio: 8/1) 86wt% using a normal pentane solvent, purification processing of the DAO was carried out on the following hydrotreating conditions, and comparative refined oil B was obtained.

40 hydrotreating -- conditions -- : -- nickel/Mo+Co/Mo -- a catalyst (it is 1/9 at a volume ratio) -- hydrogen -- a partial pressure -- : -- 90 -- [-- atm --] -- H -- two -- /-- Oil -- : -- 600 -- [-- Nm -- three -- /-- kl --] -- temperature -- : -- 360 -- degree C -- LHSV -- : -- 0.5 -- [-- one -- /-- hr --] -- obtaining -- having had -- DAO -- and -- refined oil -- B -- stock oil -- receiving -- a yield -- a hydrogen content -- each -- a process -- it can set -- a hydrogen content -- augend -- V+nickel -- a

5 content -- CCR -- sulfur -- concentration -- Table 2 -- be shown .

10 [0045] After having carried out extraction separation, carrying out and obtaining DAO using the same stock oil as example of comparison 3 example 1 so that it may become extractability (solvent/Oil ratio: 8/1) 81wt% using a normal pentane solvent, purification processing of the DAO was carried out on the following hydrotreating conditions, and comparative refined oil C was obtained.

15 hydrotreating -- conditions -- : -- nickel/Mo+Co/Mo -- a catalyst (it is 1/9 at a volume ratio) -- hydrogen -- a partial pressure -- : -- 90 -- [-- atm --] -- H -- two -- /-- Oil -- : -- 600 -- [-- Nm -- three -- /-- kl --] -- temperature -- : -- 345 -- degree C -- LHSV -- : -- 0.6 -- [-- one -- /-- hr --] -- obtaining -- having had -- DAO -- and -- refined oil -- C -- stock oil -- receiving -- a yield -- a hydrogen content -- each -- a process -- it can set -- a hydrogen content -- augend -- V+nickel -- a content -- CCR -- sulfur -- concentration -- Table 2 -- be shown .

20 [0046] Using the same stock oil as example of comparison 4 example 1, extraction separation was carried out and comparative refined oil D was obtained so that it might become extractability (solvent/Oil ratio: 8/1) 45wt% using a propane solvent. The augend of the yield to the stock oil of the obtained refined oil D, a hydrogen content, and the hydrogen content in each process, a V+nickel content, CCR, and sulfur concentration are shown in Table 2.

25 [0047] Using the same stock oil as example of comparison 5 example 1, purification processing was carried out on the following hydrotreating conditions, and comparative refined oil E was obtained.

30 hydrotreating -- conditions -- : -- nickel/Mo+Co/Mo -- a catalyst (it is 1/9 at a volume ratio) -- hydrogen -- a partial pressure -- : -- 150 -- [-- atm --] -- H -- two -- /-- Oil -- : -- 1000 -- [-- Nm -- three -- /-- kl --] -- temperature -- : -- 380 -- degree C -- LHSV -- : -- 0.25 -- [-- one -- /-- hr --] -- obtaining -- having had -- refined oil -- E -- stock oil -- receiving -- a yield -- a hydrogen content -- each -- a process -- it can set -- a hydrogen content -- augend -- V+nickel -- a content -- CCR -- sulfur -- concentration -- Table 2 -- be shown -- .

35 [0048]
[Table 2]

| | 原料油 | 比較1 | | 比較2 | | 比較3 | | 比較4 | 比較5 |
|----------------|-------|----------|-------|----------|-------|----------|-------|----------|-----------|
| | | DAO 精製油A | | DAO 精製油B | | DAO 精製油C | | D (抽出のみ) | E (水素化のみ) |
| 得率 (wt%) | 100 | 88 | 84 | 86 | 82 | 81 | 77 | 45 | 95 |
| 水素含有量 (wt%) | 11.25 | 11.37 | 11.79 | 11.40 | 12.08 | 11.55 | 11.90 | 11.95 | 12.10 |
| 水素含有量増加量 (wt%) | — | 0.15 | 0.42 | 0.15 | 0.68 | 0.30 | 0.35 | 0.70 | 0.85 |
| 合計水素増加量 (wt%) | — | — | 0.54 | — | 0.83 | — | 0.65 | — | — |
| V+Ni (wt ppm) | 65.0 | 16.8 | <0.1 | 13.5 | <0.1 | 7.3 | <0.1 | 2.0 | 7.0 |
| ジストル残留炭素 (wt%) | 11.10 | 4.30 | 1.47 | 3.70 | 0.81 | 2.60 | 1.21 | 0.50 | 5.70 |
| S (wt%) | 3.95 | 3.57 | 1.03 | 3.51 | 0.32 | 3.35 | 0.83 | 3.07 | 0.50 |

40 [0049] It pyrolyzed on condition that the following, using respectively the last refined oil obtained in the example examples 1-4 of low-grade olefin manufacture, and the examples 1-5 of a comparison.

Reaction condition: Coil : It is use feeding about bore 28mmphi and HPM material ethylene

5 decomposition tubing with a die length of 1440mm (heating unit 1200mm per part). : Stock oil =
 1.69 [L/Hr] and water are adjustment reaction temperature about the amount of supply so that it
 may be set to 1.0 by the weight ratio to stock oil. : 900-degree-C pressure : Ordinary pressure
 residence time : It asked for the yield of the low-grade olefin (ethylene and propylene) obtained
 10 for 0.5 seconds from the gas presentation in the generation gas analyzed using generation
 capacity and a gas chromatograph. The amount of generation of byproduction heavy oil
 calculated the generation oil after cooling cracked gas from the bottom oil quantity after
 separating a naphtha fraction by distillation. Moreover, decision of continuous-running nature is
 a generation weight ratio to stock oil, and judged the byproduction heavy oil leading to fouling
 which deposited in the sudden cooling section which branches from a coil as less than [30wt%]
 15 =O and more than 30wt%=x. A result is shown in Table 3.

[0050]

[Table 3]

| | 実施例 1 | 実施例 2 | 実施例 3 | 実施例 4 | 比較 A | 比較 B | 比較 C | 比較 D | 比較 E |
|---------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 水素含有量 (wt%) | 12.33 | 12.28 | 12.14 | 12.65 | 11.79 | 12.08 | 11.90 | 11.95 | 12.10 |
| エチレン収率 (wt%) | 16.7 | 16.1 | 15.9 | 18.1 | 11.5 | 13.1 | 13.4 | 13.1 | 14.0 |
| プロピレン収率 (wt%) | 13.1 | 12.5 | 12.2 | 14.8 | 8.5 | 9.7 | 10.2 | 10.1 | 10.4 |
| 副生重質油 (wt%) | 28.1 | 28.7 | 29.5 | 24.5 | 36.5 | 33.2 | 34.8 | 34.6 | 32.9 |
| 連続運転性 | ○ | ○ | ○ | ○ | × | × | × | × | × |

20 [0051] DAO obtained by solvent extraction processing in the examples 1-4 of this invention --
 heavy stock oil -- comparing -- a hydrogen content -- more than 0.2wt% -- the hydrorefining oil
 which extracts so that it may increase, and continues -- DAO -- comparing -- a hydrogen content
 -- more than 0.5wt% -- it increases -- as -- processing -- as a result -- the last refined oil -- heavy
 25 stock oil -- comparing -- more than 0.7wt% -- it processed so that it might increase. In the refined
 oil of this invention, as for V+nickel, the refined oil from which the impurity was removed for
 0.1 or less wtppms and KONRADOSON carbon residue by less than [0.8wt%] and less than [
 sulfur concentration 0.3wt%] was obtained by each. On the other hand, the KONRADOSON
 carbon residue of the last refined oil is more than 0.8wt%, and the sulfur concentration of the
 30 examples 1-5 of a comparison with which are not satisfied of the increment in the hydrogen
 content of this invention is more than 0.3wt%.

[0052] It turns out only especially by solvent extraction processing that sulfur concentration does
 not fall even if it makes extractability of DAO small, and KONRADOSON carbon residue is not
 35 removable only by hydrorefining processing even if it increases hydrogen consumption sharply.
 Moreover, by the result of having carried out pyrolysis processing of the obtained refined oil,
 and having manufactured the low-grade olefin, by the refined oil of this invention, ethylene yield
 all exceeded 15%, propylene yield is over 10% and continuous-running nature was further
 judged to be the possible range from the generation situation of byproduction heavy oil. On the
 40 other hand, in the example of a comparison with which are not satisfied of this invention,
 ethylene yield does not exceed 15%, but further, there are many amounts of generation of
 byproduction heavy oil, and it turns out that each continuous-running nature has a problem.

[0053] It introduced into the solvent extraction processor by making into stock oil the heavy oil
 45 (hydrogen content: 10.68wt% and nickel+V metal:246wtppm, CCR:25wt%, and S:5.5wt%)
 which is a residue oil of example 5 API gravity 4.2, and after carrying out extraction separation

5 and obtaining DAO so that it may become extractability (solvent/Oil ratio: 8/1) 63wt% using an isobutane solvent, hydrotreating of the DAO was carried out on condition that the following, and the refined oil 5 of this invention was obtained.

hydrotreating condition: -- nickel/Co/Mo+Co/Mo catalyst (it is 2/8 at volume ratio), and hydrogen partial pressure: 110[atm] H₂ / Oil ratio: -- 800 [Nm³/kl] and temperature: -- 380
10 degrees C of the augend of DAO LHSV: 0.3 [1/hr] obtained and the yield to the stock oil of refined oil 5, a hydrogen content, and the hydrogen content in each process, V+nickel contents, CCR(s), and sulfur concentration are shown in Table 4.

15 [0054] After carrying out extraction separation and obtaining DAO using the same stock oil as example 6 example 5 so that it may become extractability (solvent/Oil ratio: 8/1) 65wt% using an isobutane solvent, purification processing of the DAO was carried out on the following hydrotreating conditions, and the refined oil 6 of this invention was obtained.

hydrotreating -- conditions -- : -- nickel/Mo+Co/Mo -- a catalyst (it is 2/8 at a volume ratio) -- hydrogen -- a partial pressure -- : -- 140 -- [-- atm --] -- H -- two -- /-- Oil -- : -- 1000 -- [-- Nm --
20 three -- /-- kl --] -- temperature -- : -- 375 -- degree C -- LHSV -- : -- 0.2 -- [-- one -- /-- hr --] -- obtaining -- having had -- DAO -- and -- refined oil -- six -- stock oil -- receiving -- a yield -- a hydrogen content -- each -- a process -- it can set -- a hydrogen content -- augend -- V+nickel -- a content -- CCR -- sulfur -- concentration -- Table 4 -- be shown .

25 [0055]
[Table 4]

| | 原料油 | 実施例5 | | 実施例6 | |
|----------------|-------|-------|-------|-------|-------|
| | | DAO | 精製油5 | DAO | 精製油6 |
| 得率 (wt%) | 100 | 63 | 59 | 65 | 59 |
| 水素含有量 (wt%) | 10.68 | 11.83 | 12.71 | 11.68 | 12.96 |
| 水素含有量増加量 (wt%) | — | 1.15 | 0.88 | 1.00 | 1.28 |
| 合計水素増加量 (wt%) | — | — | 2.03 | — | 2.28 |
| V+Ni (wt ppm) | 246.0 | 41.0 | <0.1 | 45.0 | <0.1 |
| ナフテン残留炭素 (wt%) | 25.00 | 11.60 | 0.56 | 11.90 | 0.36 |
| S (wt%) | 5.50 | 4.30 | 0.20 | 4.32 | 0.13 |

30 [0056] After carrying out extraction separation and obtaining DAO using the same stock oil as example of comparison 6 example 5 so that it may become extractability (solvent/Oil ratio: 8/1) 65wt% using an isobutane solvent, purification processing of the DAO was carried out on the following hydrotreating conditions, and comparative refined oil F was obtained.

hydrotreating -- conditions -- : -- nickel/Mo+Co/Mo -- a catalyst (it is 2/8 at a volume ratio) -- hydrogen -- a partial pressure -- : -- 80 -- [-- atm --] -- H -- two -- /-- Oil -- : -- 800 -- [-- Nm --
35 three -- /-- kl --] -- temperature -- : -- 340 -- degree C -- LHSV -- : -- 0.5 -- [-- one -- /-- hr --] -- obtaining -- having had -- DAO -- and -- refined oil -- F -- stock oil -- receiving -- a yield -- a hydrogen content -- each -- a process -- it can set -- a hydrogen content -- augend -- V+nickel -- a content -- CCR -- sulfur -- concentration -- Table 5 -- be shown .

40 [0057] Using the same stock oil as example of comparison 7 example 5, extraction separation was carried out and comparative refined oil G was obtained so that it might become extractability (solvent/Oil ratio: 8/1) 55wt% using an isobutane solvent. The augend of the yield to the stock oil of the obtained refined oil G, a hydrogen content, and the hydrogen content in

5 each process, a V+nickel content, CCR, and sulfur concentration are shown in Table 5.

[0058] Using the same stock oil as example of comparison 8 example 5, purification processing was carried out on the following hydrotreating conditions, and comparative refined oil H was obtained.

10 hydrotreating -- conditions -- : -- nickel/Mo+Co/Mo -- a catalyst (it is 3/7 at a volume ratio) -- hydrogen -- a partial pressure -- : -- 140 -- [atm] -- H -- two -- / -- Oil -- : -- 1000 -- [Nm -- three -- / -- kl] -- temperature -- : -- 375 -- degree C -- LHSV -- : -- 0.2 -- [one -- / -- hr] -- obtaining -- having had -- refined oil -- H -- stock oil -- receiving -- a yield -- a hydrogen content -- each -- a process -- it can set -- a hydrogen content -- augend -- V+nickel -- a content -- CCR --
15 sulfur -- concentration -- Table 5 -- be shown -- .

[0059]

[Table 5]

| | 原料油 | 比較6 | | 比較7 | 比較8 |
|----------------|-------|-------|-------|----------|-----------|
| | | DAO | 精製油F | G (抽出のみ) | H (水素化のみ) |
| 得率 (wt%) | 100 | 65 | 61 | 55 | 91 |
| 水素含有量 (wt%) | 10.68 | 11.68 | 12.08 | 11.88 | 11.69 |
| 水素含有量増加量 (wt%) | — | 1.00 | 0.40 | 1.20 | 1.01 |
| 合計水素増加量 (wt%) | — | — | 1.40 | 1.20 | 1.01 |
| V+Ni (wtppm) | 246.0 | 45.0 | <0.1 | 26.0 | 32.0 |
| アサリ残留炭素 (wt%) | 25.00 | 12.20 | 3.91 | 9.20 | 9.25 |
| S (wt%) | 5.50 | 4.32 | 2.60 | 4.09 | 1.31 |

20 [0060] Using respectively the last refined oil obtained in the example examples 5-6 of low-grade olefin manufacture, and the examples 6-8 of a comparison, it pyrolyzes on the same conditions as the above, and the yield of the obtained low-grade olefin, the yield of byproduction heavy oil, and the decision result of continuous-running nature are shown in Table 6.

25 [0061]
[Table 6]

| | 実施例5 | 実施例6 | 比較6 | 比較7 | 比較8 |
|---------------|-------|-------|-------|-------|-------|
| 水素含有量 (wt%) | 12.71 | 12.96 | 12.08 | 11.88 | 11.69 |
| エチレン収率 (wt%) | 18.1 | 19.1 | 13.5 | 13.1 | 12.1 |
| プロピレン収率 (wt%) | 14.7 | 15.2 | 9.4 | 9.1 | 8.6 |
| 副生重質油 (wt%) | 25.0 | 23.8 | 33.2 | 35.9 | 36.1 |
| 連続運転性 | ○ | ○ | × | × | × |

30 [0062] the examples 5-6 of this invention -- solvent extraction down stream processing -- setting -- heavy stock oil -- comparing -- a hydrogen content -- more than 0.2wt% -- hydrotreating down stream processing which extracts so that it may increase, and continues -- setting -- DAO -- comparing -- a hydrogen content -- more than 0.5wt% -- it increases -- as -- processing -- **** --
35 as a result -- the last refined oil -- stock oil -- receiving -- more than 0.7wt% -- it is increasing. In the refined oil of obtained this invention, as for 0.1 or less wtppms and CCR, the nickel+V concentration of less than [1wt%] and sulfur concentration is less than [0.5wt%], and the refined oil of the high quality from which the impurity was removed by altitude is obtained by

5 each.

10 [0063] On the other hand, in the comparison 7 refined only by solvent extraction processing, recovery is made low even to 55% and it turns out that removal of an impurity is not enough even if it carries out extract purification. moreover, although hydrorefining is the same conditions when the example 6 of this invention is compared with the comparison 8 refined only by hydrorefining, after it turning out that a big difference is in removal of an impurity and increasing a predetermined hydrogen content by solvent extraction processing beforehand, by carrying out hydrorefining processing shows that it is markedly alike, an impurity is removed and the refined oil of high quality is obtained. Furthermore, by the result of having carried out pyrolysis processing of the obtained refined oil, and having manufactured the low-grade olefin, by the refined oil of this invention, ethylene yield exceeded 15%, propylene yield is over 10% and continuous-running nature was further judged to be the possible range from the generation situation of byproduction heavy oil. On the other hand, in the example of a comparison with which are not satisfied of this invention, ethylene yield does not exceed 15%, but further, there are many amounts of generation of byproduction heavy oil, and it turns out that each continuous-running nature has a problem.

25 [0064] Distillation separated into the distillate and the residue oil the ARABIAN heavy crude oil of manufacture API gravity 27.4 of the refined oil which used example 10 heavy crude as the start base, hydrorefining of a part of distillate was carried out, and GO was obtained. On the other hand, solvent extraction processing and hydrorefining processing were carried out on the same conditions as the example 1 of this invention by having made into stock oil 1 the heavy oil of API gravity 10.9 which is a residue oil, and refined oil 10 was obtained. A part of stock oil 2 (they are 10 weight sections to the crude oil 100 weight section) was mixed, a part of this refined oil 10 (they are 20 weight sections to the crude oil 100 weight section) and Above GO were used as a pyrolysis raw material for low-grade olefin manufacture, and the low-grade olefin was manufactured. The yield of the ordinary pressure residual oil of an example 10, a deasphaltene oil, a hydrorefining deasphaltene oil, and a heavy ethylene raw material, a hydrogen content, a nickel+V metal content, a CCR content, and S content are shown in Table 7.

35 [0065]

[Table 7]

| | 原料油 1 | | | 原料油 2 | 原料油 (1+2) |
|-------------------|-------|-------|-------|-------|----------------------|
| | 常圧残油 | DAO | 精製油10 | GO | 精製油 10 : 20, GO : 10 |
| 得率 (wt%) (原油=100) | 61 | 49 | 45 | 18 | 30 |
| 水素含有量 (wt%) | 11.20 | 11.42 | 11.95 | 13.70 | 12.53 |
| 水素含有量増加量 (wt%) | — | 0.22 | 0.53 | — | — |
| 合計水素増加量 (wt%) | — | — | 0.75 | — | — |
| V+Ni (wt ppm) | 153.0 | 14.2 | 0.7 | <0.1 | <0.1 |
| コナドの残留炭素 (wt%) | 12.50 | 3.60 | 1.90 | 0.00 | 1.20 |
| S (wt%) | 4.70 | 3.50 | 0.40 | 0.05 | 0.27 |
| エチレン収率 (wt%) | — | — | — | — | 17.6 |
| プロピレン収率 (wt%) | — | — | — | — | 14.1 |
| 副生重質油 (wt%) | — | — | — | — | 25.8 |
| 連続運転性 | — | — | — | — | ○ |

40 [0066] It has checked that it was the result of mixing a distillate with the low high impurity

- 5 concentration separately prepared to the refined oil obtained by performing purification processing of this invention by making a residue oil into stock oil, considering as the raw material for low-grade olefin manufacture, and being able to be satisfied with an example 10 of both the yield of ethylene and a propylene, and continuous-running nature.

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(54) 【発明の名称】 重質油の精製方法

(57) 【要約】

【課題】 安価な重質油を原料とし、簡単で確実な方法で、経済性に優れた重質油の精製方法の提供。

【解決手段】 水素含有量が12wt%以下の重質油を原料油として、水素含有量が原料油に対して0.2wt%以上増加するように溶剤抽出処理した後、水素含有量が抽出油に対して0.5wt%以上増加するように水素化精製処理して精製油を得ることを特徴とする重質油の精製方法。

【特許請求の範囲】

【請求項1】 原料油を、溶剤抽出処理して抽出油を得る溶剤抽出工程と、得られた抽出油を水素と触媒の存在下に水素化処理して精製油を得る水素化精製工程とを含む処理により精製油を得る重質油の精製方法であって、原料油は、水素含有量が12wt%以下の重質油であり、その原料油を溶剤抽出工程に導入し、水素含有量が原料油に対して0.2wt%以上増加するように溶剤抽出処理して抽出油である脱アスファルテン油(DAO)を得る溶剤抽出工程と、脱アスファルテン油を水素化精製工程に導入し、水素含有量が脱アスファルテン油に対して0.5wt%以上増加するように水素化精製して精製油を得る水素化精製工程とを有することを特徴とする重質油の精製方法。

【請求項2】 原料油を、溶剤抽出処理して抽出油を得る溶剤抽出工程と、得られた抽出油を水素と触媒の存在下に水素化処理して精製油を得る水素化精製工程とを含む処理により精製油を得る重質油の精製方法であって、原料油は、水素含有量が12wt%以下の重質油であり、その原料油を溶剤抽出工程に導入し、水素含有量が重質油に対して0.2wt%以上増加するように溶剤抽出処理して抽出油である脱アスファルテン油(DAO)を得る溶剤抽出工程と、脱アスファルテン油を水素化精製工程に導入し、水素含有量が脱アスファルテン油に対して0.5wt%以上増加するように水素化精製して精製油を得る水素化精製工程とを有し、水素化精製工程で得られる水素含有量が原料油に対して0.7wt%以上増加した精製油の水素含有量が、11.5wt%以上であることを特徴とする重質油の精製方法。

【請求項3】 溶剤抽出工程で得られる脱アスファルテン油の原料油に対する水素含有量の増加が、0.2～1.5wt%であり、水素化精製工程で得られる精製油の脱アスファルテン油に対する水素含有量の増加が、0.5～1.5wt%である請求項1または2の重質油の精製方法。

【請求項4】 前記原料油の水素含有量が11～12wt%であり、溶剤抽出工程で得られる脱アスファルテン油の原料油に対する水素含有量の増加が、0.2～1.0wt%であり、水素化精製工程で得られる精製油の脱アスファルテン油に対する水素含有量の増加が、0.5～1.0wt%である請求項1～3のいずれか1項記載の重質油の精製方法。

【請求項5】 前記原料油の水素含有量が11wt%未満であり、溶剤抽出工程で得られる脱アスファルテン油の原料油に対する水素含有量の増加が、0.5～1.5wt%であり、水素化精製工程で得られる精製油の脱アスファルテン油に対する水素含有量の増加が、0.6～1.5wt%である請求項1～4のいずれか1項記載の重質油の精製方法。

【請求項6】 前記脱アスファルテン油中のNiとVの

合計量が70wtppm以下でコンラドソン残留炭素が15wt%以下となるように溶剤抽出処理する請求項1～5のいずれか1項記載の記載の重質油の精製方法。

【請求項7】 溶剤抽出工程と水素化精製工程で処理して得られた精製油のV+Niの含有量が2wtppm以下であり、コンラドソン残留炭素含有量が1wt%以下であり、硫黄含有量が0.5wt%以下である請求項1～6のいずれか1項記載の重質油の精製方法。

【請求項8】 前記精製油の少なくとも一部を低級オレフィン製造用熱分解原料油として用いるとともに、その熱分解原料油中の水素含有量が12.0wt%以上である請求項1～7のいずれか1項記載の重質油の精製方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、原油起源の不純物を効率的に除去できる溶剤抽出処理と水素化精製処理とによる重質油の精製方法に関し、特に、従来、低級オレフィン製造用原料に用いられなかった重質油から低級オレフィン製造用原料にも適した精製油を得ることができ重質油の精製方法に関する。

【0002】

【従来の技術及び発明が解決しようとする課題】原油を出発物質とする石油製品は、原油中にその起源に由来する不純物が存在するため、常圧および減圧蒸留分離を始めとした物理的または化学的な各種の精製処理を施して生産されている。一般に、石油留分すなわち、蒸留により塔頂から分離される留出油は、上記不純物が少なく、簡単な精製処理で不純物を除去できることから、高度に不純物が除去された高品質の石油製品である自動車燃料やガスタービン燃料等の高級燃料油や石油化学用原料等として利用されている。

【0003】一方、蒸留残渣油等の重質油に関しては、不純物が濃縮されてその量が多いだけでなく、非常に除去されにくい形態で存在しており、基本的な精製手段である水素化精製ではその不純物除去に限界がある。特に高度に精製する場合には、水素と触媒の存在下で高温・高圧の過酷な反応条件が要求され、多量の水素や触媒を消費しかつ、設備費も含め多額の投資が必要となり経済的でないのが現状である。したがって、重質油から付加価値が高い、すなわち高度に不純物が除去された高品質な精製油を簡便に、かつ経済的に得る方法が待望されている。

【0004】高品質な精製油は、その用途の一つとして石油化学用の原料としての利用がある。石油化学分野の基幹物質であるエチレンやプロピレン等の低級オレフィン、エタンやナフサ等の軽質油が主な原料として熱分解により製造されているが、一部で軽質油や減圧軽油などの重質な留分も原料としても利用されている。天然ガスが豊富で安価な米国や中東では前者のエタンを原

料としたエチレンプラントが主流であるが、ナフサの方が安価な日本、アジア、ヨーロッパでは、後者のナフサを原料とする場合がほとんどである。

【0005】ナフサを原料としたエチレンプラントでは、タール、ピッチなどの副生成物の生成がエタンを原料とした場合より多くなるため、主反応器である熱分解管、その後段の急冷熱交換器でのコーキングやファウリングへの対応が必要となる。そして、ナフサより分子量の大きく、金属や硫黄分が多い減圧軽油がエチレンプラントの原料として、商業運転が可能な限界と考えられて

いる。
【0006】一方、原料供給量および原料コストの観点から、軽油留分より重質な原料油を低級オレフィン製造用原料として用いることができれば、原料コストが安価であるとともに石油資源の重質化に伴う原料油の安定供給上の問題も解決できることとなり、産業上極めて大きな貢献となる。

【0007】本発明は、上記の状況に鑑みて為されたものであり、原油起源の不純物を高い濃度で含有する重質油から付加価値の高い精製油を経済的に回収する方法を提供するものであり、特に低級オレフィン用原料としては従来不適とされてきた常圧残渣などの重質油を簡単に確実な方法で精製処理することにより、経済的に低級オレフィン製造用原料にも適した精製油を回収することができる重質油の精製方法を提供することである。

【0008】

【課題を解決するための手段】本発明者らは、上記目的を達成すべく鋭意研究した結果、水素含有量が12wt%以下の重質油を原料とし、溶剤抽出により水素含有量を一定量以上増加するよう処理し、続いて、得られた脱アスファルテン油を水素化精製処理により水素含有量を一定量以上増加するよう処理することにより、重質油中の不純物が効率的に除去でき、高度に不純物が除去された高品質の精製油が得られることを見出し、本発明を完成した。

【0009】すなわち、本発明は、原料油を、溶剤抽出処理して抽出油を得る溶剤抽出工程と、得られた抽出油を水素と触媒の存在下に水素化処理して精製油を得る水素化精製工程とを含む処理により精製油を得る重質油の精製方法であって、原料油は、水素含有量が12wt%以下の重質油であり、その原料油を溶剤抽出工程に導入し、水素含有量が原料油に対して0.2wt%以上増加するように溶剤抽出処理して抽出油である脱アスファルテン油(DAO)を得る溶剤抽出工程と、脱アスファルテン油を水素化精製工程に導入し、水素含有量が脱アスファルテン油に対して0.5wt%以上増加するように水素化精製して精製油を得る水素化精製工程とを有することを特徴とする重質油の精製方法を提供するものである。

【0010】かかる構成をとることにより、後段の水素

化精製で除去されにくい不純物を予め溶剤抽出により一定量以上水素含有量が増加する条件で処理し、その後に水素化精製工程により一定量以上水素含有量が増加する条件で処理するため、それぞれの精製工程単独では予想できない高度に不純物が除去された高品質の精製油を、確実に得ることができる。本発明者等は、溶剤抽出工程と水素化精製処理とを単純に実施するだけでは、不純物を確実に実施できないことに着目し、処理する重質油の水素含有量を指標として、溶剤抽出工程とそれに続く水素化精製工程でそれぞれ所定量の水素含有量を増加させるように処理することにより、確実に、かつ効率的に高度に不純物が除去された精製油を得ることができることを見出したものであり、溶剤抽出工程と水素化精製工程の条件を過酷な条件とすることがなく、負荷のバランスが保たれる経済的な条件で得ることができる。

【0011】さらに本発明においては、上記で得られた精製油の水素含有量が11.5wt%以上、好ましくは12.0wt%以上であることを特徴とする重質油の精製方法を提供するものである。これにより得られた精製油は、石油化学用原料である低級オレフィン製造用原料に適用した場合には、熱分解反応の際にもコーキングやファウリングの発生が抑えられて商業運転が可能となるものである。かかる理由から、本発明の精製方法は、付加価値の高い精製油を確実に、かつ効率的に得ることができる経済的に優れた方法である。

【0012】

【発明の実施の形態】本発明は、水素含有量が12wt%以下、好ましくは10～12wt%の重質油を原料として、溶剤抽出工程と水素化精製処理工程においてそれぞれ所定の精製度を達成する条件でそれぞれ処理する。本発明に用いる12wt%以下の重質油は、一般に常圧残渣油等の残渣油、超重質原油等が相当し、不純物濃度が高いためその用途が限定されていた。これら重質油の水素含有量は、一般に9～12.5重量%、多くは9～11.5重量%であり、従来は精製しても不純物が充分には除去できず低級オレフィン用などの石油化学用原料には不適とされて用いられてなかった。

【0013】本発明は、水素含有量が12wt%以下の重質油を原料油として、第1の工程として溶剤抽出処理を行い、水素含有量を0.2wt%以上増加した抽出油である脱アスファルテン油を回収する。この溶剤抽出処理工程では、水素含有量が少ないアスファルテン分を選択的に除去する。このアスファルテン分は、縮合多環芳香族やシクロパラフィン環などの水素含有量が少ない化合物からなるミセル構造をしており、その内部には残留炭素やV、Niなどの金属類のポルフィリン化合物が含有され、不純物が濃縮されていることが知られている。そしてアスファルテン分は、水素化精製反応を著しく抑制し、触媒の劣化を促進させることも知られており、本発明においては水素含有量が0.2wt%以上増加する

条件で溶剤抽出処理することにより、その結果アスファルテンの所定量を選択的に除去する。

【0014】溶剤抽出処理は、従来知られている溶剤脱歴処理が適用でき、重質油を溶剤抽出塔においてC3～C5の溶剤と向流接触させることにより、脱アスファルテン油と、水素含有量が少なくかつメタルや残留炭素が濃縮されているアスファルテンとに分離する。そして、用いる溶剤の種類や重質油に対する溶剤量、抽出温度条件を適宜に選択することにより、水素含有量を0.2wt%以上増加するように抽出処理条件を制御して本発明の抽出油を得ることができる。C3～C5の溶剤としては、プロパン、ブタン、ペンタンから選ばれる少なくとも一つが好ましく用いられる。

【0015】脱アスファルテン油は、抽出塔の塔頂部から溶剤とともに抽出液として回収し、抽出液中の溶剤を超臨界状態で分離除去することによって得ることができる。アスファルテンについては、これを塔底部から一部の溶剤とともに抽残液として回収し、抽残液中の溶剤を蒸発によって回収する。

【0016】本発明においては、かかる溶剤抽出処理工程で得られた脱アスファルテン油の水素含有量は、原料重質油の水素含有量より0.2wt%以上増加している。さらに、0.2～1.5wt%増加することが好ましく、0.2～1.2wt%増加することが特に好ましい。

【0017】さらに、原料重質油の水素含有量の値により、溶剤抽出処理の水素含有量の増加量を変えることが好ましい。すなわち、原料油の水素含有量が11wt%以上の場合には、溶剤抽出工程において原料油に対して0.2～1.0wt%、特に0.2～0.5wt%の水素含有量増加になるように抽出処理条件を制御することが好ましい。また、水素含有量が11.0wt%未満であれば、0.5～1.5wt%、特に0.8～1.3wt%の範囲の増加量が好ましい。

【0018】溶剤抽出工程における水素含有量の増加は、0.2wt%以下であると不純物であるアスファルテンの除去が不十分となり、後段の水素化精製工程で処理しても不純物の除去が十分にできなくなるため必須の条件である。一方、その増加量の上限は精製度の観点からは大きければ大きいほどよいが、1.5wt%以上増加させる場合には脱アスファルテン油の回収率が低下するため経済的でない。

【0019】本発明は、上記の溶剤抽出処理で水素含有量が0.2wt%以上増加するように溶剤抽出処理した脱アスファルテン油を、続く第2の工程として水素化精製処理する。本発明の水素化精製処理においては、水素含有量が0.5wt%以上増加する条件で処理する。この水素化精製処理は、触媒と水素の存在下、高温高压で炭化水素を処理する代表的な精製処理であり、水素化分解、水素化脱硫、水素化脱金属、水素化脱窒素等の反応

のすべてを含むことができる。すなわち、原料重質油から低分子量精製油を得る水素化分解、炭化水素中の硫黄化合物を水素と反応させ、硫化水素にして分離し、原料油より低硫黄濃度の精製油を得る水素化脱硫、高温高压水素下で炭化水素中にある金属化合物を水素化し、元素状の金属にして触媒上に沈着させ、低金属濃度の精製油を得る水素化脱金属、高温高压水素下で炭化水素中の窒素化合物を水素と反応させ、アンモニアにして分離し、原料油から低窒素濃度の精製油を得る水素化脱窒素等の反応の総てを含んでもよい。

【0020】重質油には不純物として硫黄分、金属等が含まれるが、前段の溶剤抽出処理工程で予め水素化精製工程のみで除去することが困難な不純物を除去しているため、過酷な条件にすることなく効率的に、不純物を低濃度まで除去できる。本発明の水素化精製処理に用いられる触媒としては、水素化脱金属触媒、水素化脱硫触媒、水素化脱硫脱金属触媒、水素化分解触媒から選ばれる少なくとも2種類を組み合わせて用いることが好ましい。水素化精製に用いる触媒として好ましくは、Co/Mo、Ni/Co/Mo、Ni/Mo系である。

【0021】水素化精製反応の条件に特に制限はないが、一般的に行われている水素化精製反応条件の範囲が好ましい。すなわち、水素分圧は60～150kg/cm²が好ましく、80～130kg/cm²が特に好ましい。また、水素/油比は、400～1200Nm³/klが好ましく、600～1000Nm³/klが特に好ましい。LHSVは、0.1～1.0/hrが好ましく、0.2～0.8/hrが特に好ましい。反応温度は、340～440℃が好ましく、350～420℃が特に好ましい。

【0022】かかる条件は水素化精製の一般的条件であり、本発明においては前段の溶剤抽出工程の後に水素含有量が0.5wt%以上増加する条件で水素化精製工程を行えば、最終精製油としての不純物を効率的に除去することができる。本発明においては、原料油の水素含有量が11～12wt%である場合、水素化精製工程で得られる精製油の脱アスファルテン油に対する水素含有量の増加は、0.5～1.0wt%、特に0.5～0.9wt%であることが好ましい。また、原料油の水素含有量が11wt%未満である場合、水素化精製工程で得られる精製油の脱アスファルテン油に対する水素含有量の増加は、0.6～1.5wt%、特に0.8～1.3wt%であることが好ましい。

【0023】さらに、本発明の水素化精製処理工程における水素含有量の増加量は、前段の溶剤抽出工程で得られた脱アスファルテン油の水素含有量が11.5wt%以上であれば、0.5～1.0wt%の増加量であることが好ましく、11.5wt%未満であれば0.6～1.5wt%の増加量であることが好ましい。水素化精製処理工程で水素含有量の増加量が0.5wt%未満で

あると、脱アスファルテン油の不純物除去が不十分になり、1.5wt%以上の増加量にする場合には、水素分圧、反応温度、触媒充填量等の水素化精製反応の処理条件を過酷にしなければならないため経済的でない。

【0024】すなわち、水素化精製の反応条件の観点から述べれば、溶剤抽出処理工程において、水素化精製処理工程で除去されにくい不純物であるアスファルテン分を予め選択的に除去することにより、続く水素化精製処理工程において、水素分圧や反応温度を極端に高くすることなく、また触媒量を大幅に増加させて反応時間を長くしなくても不純物を効率的に低濃度まで除去できることとなる。その結果、アスファルテン中に濃縮されて除去されにくい形態で存在しているコンラドソン残留炭素やNiやV等の金属分が溶剤抽出によって選択的に除去され、次いで水素化精製処理では、除去されやすい形態で存在している硫黄、NiやV等の金属等の不純物を集中的に除去できるものである。

【0025】上記の本発明による精製工程で処理した精製油は、低級オレフィン製造用原料に適用して高温熱分解する場合においても、コーキングやファウリングの原因物質となる不純物は確実に、かつ効率的に低減されているため、低級オレフィンの収率および連続運転性から商業生産に適用することができる。これは従来低級オレフィン原料としては不適と考えられていた残渣油や超重質原油などの重質油を出発物質として簡便な精製により高品質な精製油を得ることができることを意味する。

【0026】また、本発明においては、上記を満足する条件で処理した精製油であれば本発明の精製油として有効であるが、特に低級オレフィン製造用原料として用いる場合には、水素含有量が11.5wt%以上であることが必要であり、12.0wt%以上であることがより好ましい。

【0027】本発明においては、重質油を溶剤抽出及び水素化精製の2段階の精製により得られた精製油の水素含有量は、原料重質油より0.7重量%以上増加していることが必要であり、0.8~2.7wt%であることが好ましく、さらに1.0~2.2wt%であることが好ましい。また、低級オレフィン製造用原料として用いる場合には、最終精製油の水素含有量は、11.5wt%以上であることが好ましく、12.0~13.5wt%であることがさらに好ましい。

【0028】精製油の水素含有量が11.5wt%以上、かつ原料重質油より0.7wt%以上増加するように溶剤抽出処理及び水素化精製処理を行うことにより、各処理における特性が相互に補完され、各工程の溶剤抽出および水素化精製のための装置に過大な負荷をかけることがなく、高度に精製された精製油を高収率で得ることができ、石油化学用原料に適用した場合においてもコーキングやファウリングが生じ難くなり、高収率で石油化学用原料に適した精製油を製造することができる。

【0029】本発明の重質油を溶剤抽出処理する工程においては、その原料油の水素含有量を0.2wt%以上増加する条件で抽出操作するが、Ni+V金属は、残渣油、超重質原油中に数十~数千wtppm含まれている。これらはアスファルテンに濃縮されて存在しており、溶剤抽出工程ではアスファルテンを選択的に除去できるため、溶剤抽出処理で脱アスファルテン油中の含有量を抽出精製油である脱アスファルテン油中のNi+Vの金属濃度を70wtppm以下、特に50wtppm以下にすることが好ましい。また、残留炭素含量が15wt%以下、特に12wt%以下となるように、溶剤抽出処理を行うことが好ましい。すなわち、溶剤抽出処理で水素含有量を0.2wt%増加させるとともに、Ni+V金属濃度を70wtppm以下、コンラドソン残留炭素を15wt%以下とすることが好ましく、これにより後段の水素化精製処理の条件を過酷にすることなく、確実に不純物を除去でき、高品質の精製油を得ることができる。

【0030】また、脱アスファルテン油の硫黄濃度を5wt%以下、特に4wt%以下とすることが好ましい。それにより、続く水素化精製処理で得られる最終精製油の硫黄分を0.5wt%以下、好ましくは0.3wt%以下となるように確実に処理することができる。脱アスファルテン油のNi+V濃度を70wtppm以下、残留炭素濃度が15wt%以下、硫黄濃度が5wt%以下とすることにより、続く水素化精製処理で得られる最終精製油のNi+V濃度を2wtppm以下、好ましくは1wtppm以下、残留炭素濃度を1wt%以下、硫黄濃度を0.5wt%以下、好ましくは0.3wt%以下となるように確実に処理することができる。最終精製油の硫黄分を0.5重量%以下とすることによって、低級オレフィン用原料油として用いた場合においても熱分解装置の腐食を材料の許容範囲内に抑えることができ、実質的な低級オレフィン用原料の商業製造を可能にすることができる。

【0031】本発明においては、最終精製油のNi+V金属含有量が2wtppm以下、特に1.0wtppm以下となるように溶剤抽出処理と水素化精製処理を行うことが好ましい。溶剤抽出処理でNi+V金属含有量が70重量ppm以下になった脱アスファルテン油を、水素化精製でさらにNi+V金属含有量を1wtppm以下とすることにより、コーキングを著しく低減させることができ、高収率で精製油を得ることができ、その精製油を低級オレフィン製造用熱分解原料として用いることができる。

【0032】エチレンとプロピレンを含む低級オレフィンを熱分解反応により製造する工業的な方法においては、デコーキングや副生重質油によるファウリングに対するメンテナンス性とオレフィン収率がその経済性を左右し、特に低級オレフィンの収率25%以上が目安とな

る。さらに低級オレフィンを詳しく見れば、エチレン収率が15%以上、プロピレン収率10%以上が目安になる。

【0033】また、熱分解装置のメンテナンス性を左右するコーキングや副生重質油によるファウリングに関しては、定期的なデコーキング、クリーニングで対応している。特に、副生重質油に関しては、分解管で分解された高温の分解生成物は過度な分解を防ぐ為に下流の熱交換で急冷される際、重質油の生成量が多い場合には熱交換器や配管を閉塞し、長期連続運転を不能とする。本発明のように重質油から出発する場合には、熱分解反応における副生重質油の生成量が商業運転の目安とすることができる。

【0034】本発明で得られる精製油は、従来エチレンなどの低級オレフィン製造用原料には用いられていない水素含有量が12wt%以下の重質油を精製処理し、低級オレフィン製造用原料として提供した場合に、熱分解時におけるオレフィン収率およびコーキング特性が良好で工業生産を可能とするものである。

【0035】本発明においては、原油等の単なる蒸留分離において得られる留出油中の不純物の含有量が少ない場合、または簡単な精製で不純物の含有量を低減できる場合には、原油を出発原料として留出油と残渣油とに分離し、残渣油である常圧蒸留残渣油や減圧蒸留残渣油を上記のように溶剤抽出及び水素化精製処理して精製油とし、この精製油に上記留出油を水素化精製した少なくとも一部を混合して精製油とすることもできる。

【0036】この場合、溶剤抽出工程と水素化精製工程とが本発明の水素含有量の増加基準を満足するならば、不純物含有量の少ない留出油を混合することにより、全体の不純物濃度を減少させ、さらに精製油の供給量を増加させることができることになる。低級オレフィン製造用原料油として供給する場合には、熱分解反応におけるコーキングやファウリングがさらに生じ難くなり、商業生産を可能にすることができる。

【0037】

【実施例】次に実施例を示して本発明をさらに詳細に説明するが、本発明は以下の実施例に限定されるものではない。

【0038】実施例1～4及び比較例1～5

実施例1

API比重が14.3の残渣油である重質油(水素含有量:11.25[wt%]、Ni+V金属:65[wtppm]、コンラドソン残留炭素(以下CCRという):11.1[wt%]、S:3.95[wt%])を原料油として溶剤抽出処理装置に導入し、ノルマルペンタン溶媒を用いて(solvent/Oil比:8/1)抽出率81wt%になるように抽出分離して脱アスファルテン油(以下DAOという)を得た後、脱アスファルテン油

を以下の水素化精製条件で精製処理して本発明の精製油1を得た。

水素化精製条件: Ni/Mo+Ni/Co/Mo触媒(体積比で1/9)、水素分圧:90[atm]、H₂/Oil比:600[Nm³/kl]、温度:380℃、LHSV:0.5[1/hr]

得られた脱アスファルテン油および精製油1の原料油に対する得率、水素含有量、各工程における水素含有量の増加量、V+Ni含有量、CCR、硫黄濃度を表1に示す。水素含有量はCHN元素分析法により測定した。

【0039】実施例2

実施例1で用いた原料油を溶剤抽出処理装置に導入し、ノルマルペンタン溶媒を用いて(solvent/Oil比:8/1)抽出率84wt%になるように抽出分離して脱アスファルテン油を得た後、DAOを実施例1と同様の条件で水素化精製して本発明の精製油2を得た。得られたDAOおよび精製油2の原料油に対する得率、水素含有量、各工程における水素含有量の増加量、V+Ni含有量、CCR、硫黄濃度を表1に示す。

【0040】実施例3

実施例1で用いた原料油を溶剤抽出処理装置に導入し、ノルマルペンタン溶媒を用いて(solvent/Oil比:8/1)抽出率81wt%になるように抽出分離してDAOを得た後、DAOを以下の水素化精製条件で精製処理して本発明の精製油3を得た。

水素化精製条件: Ni/Mo+Ni/Co/Mo触媒(体積比で1/9)、水素分圧:85[atm]、H₂/Oil比:600[Nm³/kl]、温度:360℃、LHSV:0.5[1/hr]

得られたDAOおよび精製油3の原料油に対する得率、水素含有量、各工程における水素含有量の増加量、V+Ni含有量、CCR、硫黄濃度を表1に示す。

【0041】実施例4

実施例1で用いた原料油を溶剤抽出処理装置に導入し、イソブタン/ノルマルペンタン混合溶媒を用いて(solvent/Oil比:8/1)抽出率76wt%になるように抽出分離してDAOを得た後、DAOを以下の水素化精製条件で精製処理して本発明の精製油4を得た。

水素化精製条件: Ni/Mo+Ni/Co/Mo触媒(体積比で1/9)、水素分圧:110[atm]、H₂/Oil比:800[Nm³/kl]、温度:380℃、LHSV:0.3[1/hr]

得られたDAOおよび精製油3の原料油に対する得率、水素含有量、各工程における水素含有量の増加量、V+Ni含有量、CCR、硫黄濃度を表1に示す。

【0042】

【表1】

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| | 原料油 | 実施例1 | | 実施例2 | | 実施例3 | | 実施例4 | |
|----------------|-------|----------|-------|----------|-------|----------|-------|----------|-------|
| | | DAO 精製油1 | | DAO 精製油2 | | DAO 精製油3 | | DAO 精製油4 | |
| 得率 (wt%) | 100 | 81 | 77 | 84 | 79 | 81 | 78 | 76 | 72 |
| 水素含有量 (wt%) | 11.25 | 11.55 | 12.33 | 11.50 | 12.28 | 11.55 | 12.14 | 11.75 | 12.65 |
| 水素含有量増加量 (wt%) | — | 0.30 | 0.78 | 0.25 | 0.78 | 0.30 | 0.59 | 0.50 | 0.90 |
| 合計水素増加量 (wt%) | — | — | 1.08 | — | 1.03 | — | 0.89 | — | 1.40 |
| V+Ni (wtppm) | 65.0 | 7.3 | <0.1 | 10.7 | <0.1 | 7.3 | <0.1 | 3.7 | <0.1 |
| コバルト残留炭素 (wt%) | 11.10 | 2.60 | 0.41 | 3.20 | 0.62 | 2.60 | 0.76 | 1.80 | 0.21 |
| S (wt%) | 3.95 | 3.35 | 0.06 | 3.45 | 0.16 | 3.35 | 0.26 | 3.19 | 0.02 |

【0043】比較例1

実施例1と同様の原料油を用いて、溶剤抽出率を88%とした以外は実施例1と同様の抽出条件で抽出分離してDAOを得た後、DAOを以下の水素化精製条件で水素化精製して比較の精製油Aを得た。

水素化精製条件: Ni/Mo+Co/Mo触媒 (体積比で1/9)、水素分圧: 90[atm]、H₂/Oil: 600[Nm³/kl]、温度: 360℃、LHSV: 0.5[1/hr]

得られたDAOおよび精製油Aの原料油に対する得率、水素含有量、各工程における水素含有量の増加量、V+Ni含有量、CCR、硫黄濃度を表2に示す。

【0044】比較例2

実施例1と同様の原料油を用いて、ノルマルペンタン溶媒を用いて (solvent/Oil比: 8/1) 抽出率86wt%になるように抽出分離してDAOを得た後、DAOを以下の水素化精製条件で精製処理して比較の精製油Bを得た。

水素化精製条件: Ni/Mo+Co/Mo触媒 (体積比で1/9)、水素分圧: 90[atm]、H₂/Oil: 600[Nm³/kl]、温度: 360℃、LHSV: 0.5[1/hr]

得られたDAOおよび精製油Bの原料油に対する得率、水素含有量、各工程における水素含有量の増加量、V+Ni含有量、CCR、硫黄濃度を表2に示す。

【0045】比較例3

実施例1と同様の原料油を用いて、ノルマルペンタン溶媒を用いて (solvent/Oil比: 8/1) 抽出率81wt%になるように抽出分離してDAOを得た*

10* 後、DAOを以下の水素化精製条件で精製処理して比較の精製油Cを得た。

水素化精製条件: Ni/Mo+Co/Mo触媒 (体積比で1/9)、水素分圧: 90[atm]、H₂/Oil: 600[Nm³/kl]、温度: 345℃、LHSV: 0.6[1/hr]

得られたDAOおよび精製油Cの原料油に対する得率、水素含有量、各工程における水素含有量の増加量、V+Ni含有量、CCR、硫黄濃度を表2に示す。

【0046】比較例4

20 実施例1と同様の原料油を用いて、プロパン溶媒を用いて (solvent/Oil比: 8/1) 抽出率45wt%になるように抽出分離して比較の精製油Dを得た。得られた精製油Dの原料油に対する得率、水素含有量、各工程における水素含有量の増加量、V+Ni含有量、CCR、硫黄濃度を表2に示す。

【0047】比較例5

実施例1と同様の原料油を用いて、以下の水素化精製条件で精製処理して比較の精製油Eを得た。

30 水素化精製条件: Ni/Mo+Co/Mo触媒 (体積比で1/9)、水素分圧: 150[atm]、H₂/Oil: 1000[Nm³/kl]、温度: 380℃、LHSV: 0.25[1/hr]

得られた精製油Eの原料油に対する得率、水素含有量、各工程における水素含有量の増加量、V+Ni含有量、CCR、硫黄濃度を表2に示す。

【0048】

【表2】

| | 原料油 | 比較1 | | 比較2 | | 比較3 | | 比較4 | 比較5 |
|----------------|-------|----------|-------|----------|-------|----------|-------|----------|-----------|
| | | DAO 精製油A | | DAO 精製油B | | DAO 精製油C | | D (抽出のみ) | E (水素化のみ) |
| 得率 (wt%) | 100 | 88 | 84 | 86 | 82 | 81 | 77 | 45 | 95 |
| 水素含有量 (wt%) | 11.25 | 11.37 | 11.79 | 11.40 | 12.08 | 11.55 | 11.90 | 11.95 | 12.10 |
| 水素含有量増加量 (wt%) | — | 0.15 | 0.42 | 0.15 | 0.68 | 0.30 | 0.35 | 0.70 | 0.85 |
| 合計水素増加量 (wt%) | — | — | 0.54 | — | 0.83 | — | 0.65 | — | — |
| V+Ni (wtppm) | 65.0 | 16.8 | <0.1 | 13.5 | <0.1 | 7.3 | <0.1 | 2.0 | 7.0 |
| コバルト残留炭素 (wt%) | 11.10 | 4.30 | 1.47 | 3.70 | 0.81 | 2.60 | 1.21 | 0.50 | 5.70 |
| S (wt%) | 3.95 | 3.57 | 1.03 | 3.51 | 0.32 | 3.35 | 0.83 | 3.07 | 0.50 |

【0049】低級オレフィン製造例

実施例1~4及び比較例1~5で得られた最終精製油を※50 反応条件:

※それぞれ用いて、以下の条件で熱分解した。

反応管 : 内径28mmφ、長さ1440mm(加熱部分1200mm)のHPM材エチレン分解管を使用
 原料供給 : 原料油=1.69[L/Hr]、水は原料油に対して重量比で1.0になるよう供給量を調整
 反応温度 : 900℃
 圧力 : 常圧
 滞留時間 : 0.5秒
 得られた低級オレフィン(エチレンおよびプロピレン)の収率は、生成ガス量とガスクロを用いて分析した生成*

* ガス中のガス組成から求めた。副生重質油の生成量は、熱分解ガスを冷却した後の生成油を蒸留でナフサ留分を分離した後のボトム油量から求めた。また、連続運転性の判断は、反応管から分岐する急冷却部に析出したファウリングの原因となる副生重質油を原料油に対する生成重量比で、30wt%以下=○、30wt%以上=×として判定した。結果を表3に示す。

【0050】

【表3】

| | 実施例1 | 実施例2 | 実施例3 | 実施例4 | 比較A | 比較B | 比較C | 比較D | 比較E |
|--------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 水素含有量(wt%) | 12.33 | 12.28 | 12.14 | 12.65 | 11.79 | 12.08 | 11.90 | 11.95 | 12.10 |
| エチレン収率(wt%) | 16.7 | 16.1 | 15.9 | 18.1 | 11.5 | 13.1 | 13.4 | 13.1 | 14.0 |
| プロピレン収率(wt%) | 13.1 | 12.5 | 12.2 | 14.8 | 8.5 | 9.7 | 10.2 | 10.1 | 10.4 |
| 副生重質油(wt%) | 28.1 | 28.7 | 29.5 | 24.5 | 36.5 | 33.2 | 34.8 | 34.6 | 32.9 |
| 連続運転性 | ○ | ○ | ○ | ○ | × | × | × | × | × |

【0051】本発明の実施例1~4では、溶剤抽出処理により得られるDAOを重質原料油に比べて水素含有量が0.2wt%以上増加するように抽出し、続く水素化精製油ではDAOに比べて水素含有量が0.5wt%以上増加するように処理し、結果として最終精製油は重質原料油に比べて0.7wt%以上増加するように処理した。本発明の精製油においては、いずれもV+Niは0.1wtppm以下、コンラドソン残留炭素が0.8wt%以下、硫黄濃度0.3wt%以下に不純物が除去された精製油が得られた。これに対し、本発明の水素含有量の増加を満足していない比較例1~5は、最終精製油のコンラドソン残留炭素が0.8wt%以上であり、硫黄濃度は0.3wt%以上である。

【0052】特に溶剤抽出処理のみではDAOの抽出率を小さくしても硫黄濃度が下がっておらず、水素化精製処理のみでは、水素消費量を大幅に増加してもコンラドソン残留炭素が除去できていないことがわかる。また、得られた精製油を熱分解処理して低級オレフィンを製造した結果では、本発明の精製油ではいずれもエチレン収率が15%を超え、プロピレン収率は10%を超えており、さらに、副生重質油の生成状況から連続運転性は可能な範囲と判断された。一方、本発明を満足しない比較例では、エチレン収率が15%を超えておらず、さらに、副生重質油の生成量が多く連続運転性はいずれも問題があることがわかる。

【0053】実施例5

API比重4.2の残渣油である重質油(水素含有量:10.68wt%、Ni+V金属:246wtppm、※

※CCR:25wt%、S:5.5wt%)を原料油として溶剤抽出処理装置に導入し、イソブタン溶媒を用いて(solvent/Oil比:8/1)抽出率63wt%になるように抽出分離してDAOを得た後、DAOを以下の条件で水素化精製して本発明の精製油5を得た。水素化精製条件: Ni/Co/Mo+Co/Mo触媒(体積比で2/8)、水素分圧:110[atm]、H₂/Oil比:800[Nm³/kl]、温度:380℃、LHSV:0.3[1/hr]

得られたDAOおよび精製油5の原料油に対する得率、水素含有量、各工程における水素含有量の増加量、V+Ni含有量、CCR、硫黄濃度を表4に示す。

【0054】実施例6

実施例5と同様の原料油を用いて、イソブタン溶媒を用いて(solvent/Oil比:8/1)抽出率65wt%になるように抽出分離してDAOを得た後、DAOを以下の水素化精製条件で精製処理して本発明の精製油6を得た。

水素化精製条件: Ni/Mo+Co/Mo触媒(体積比で2/8)、水素分圧:140[atm]、H₂/Oil:11000[Nm³/kl]、温度:375℃、LHSV:0.2[1/hr]

得られたDAOおよび精製油6の原料油に対する得率、水素含有量、各工程における水素含有量の増加量、V+Ni含有量、CCR、硫黄濃度を表4に示す。

【0055】

【表4】

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| | 原料油 | 実施例5 | | 実施例6 | |
|----------------|-------|-------|-------|-------|-------|
| | | DAO | 精製油5 | DAO | 精製油6 |
| 得率 (wt%) | 100 | 63 | 59 | 65 | 59 |
| 水素含有量 (wt%) | 10.68 | 11.83 | 12.71 | 11.68 | 12.96 |
| 水素含有量増加量 (wt%) | — | 1.15 | 0.88 | 1.00 | 1.28 |
| 合計水素増加量 (wt%) | — | — | 2.03 | — | 2.28 |
| V+Ni (wtppm) | 246.0 | 41.0 | <0.1 | 45.0 | <0.1 |
| コバルト残留炭素 (wt%) | 25.00 | 11.60 | 0.56 | 11.90 | 0.36 |
| S (wt%) | 5.50 | 4.30 | 0.20 | 4.32 | 0.13 |

【0056】比較例6

実施例5と同様の原料油を用いて、イソブタン溶媒を用いて (solvent/Oil比: 8/1) 抽出率65 wt%になるように抽出分離してDAOを得た後、DAOを以下の水素化精製条件で精製処理して比較の精製油Fを得た。

水素化精製条件: Ni/Mo+Co/Mo触媒 (体積比で2/8)、水素分圧: 80[atm]、H₂/Oil: 800[Nm³/kl]、温度: 340℃、LHSV: 0.5[l/hr]

得られたDAOおよび精製油Fの原料油に対する得率、水素含有量、各工程における水素含有量の増加量、V+Ni含有量、CCR、硫黄濃度を表5に示す。

【0057】比較例7

実施例5と同様の原料油を用いて、イソブタン溶媒を用いて (solvent/Oil比: 8/1) 抽出率55*

*wt%になるように抽出分離して比較の精製油Gを得

た。得られた精製油Gの原料油に対する得率、水素含有量、各工程における水素含有量の増加量、V+Ni含有量、CCR、硫黄濃度を表5に示す。

【0058】比較例8

実施例5と同様の原料油を用いて、以下の水素化精製条件で精製処理して比較の精製油Hを得た。

水素化精製条件: Ni/Mo+Co/Mo触媒 (体積比で3/7)、水素分圧: 140[atm]、H₂/Oil: 1000[Nm³/kl]、温度: 375℃、LHSV: 0.2[l/hr]

得られた精製油Hの原料油に対する得率、水素含有量、各工程における水素含有量の増加量、V+Ni含有量、CCR、硫黄濃度を表5に示す。

【0059】

【表5】

| | 原料油 | 比較6 | | 比較7 | 比較8 |
|----------------|-------|-------|-------|----------|-----------|
| | | DAO | 精製油F | G (抽出のみ) | H (水素化のみ) |
| 得率 (wt%) | 100 | 65 | 61 | 55 | 91 |
| 水素含有量 (wt%) | 10.68 | 11.68 | 12.08 | 11.88 | 11.69 |
| 水素含有量増加量 (wt%) | — | 1.00 | 0.40 | 1.20 | 1.01 |
| 合計水素増加量 (wt%) | — | — | 1.40 | 1.20 | 1.01 |
| V+Ni (wtppm) | 246.0 | 45.0 | <0.1 | 26.0 | 32.0 |
| コバルト残留炭素 (wt%) | 25.00 | 12.20 | 3.91 | 9.20 | 9.25 |
| S (wt%) | 5.50 | 4.32 | 2.60 | 4.09 | 1.31 |

【0060】低級オレフィン製造例

実施例5～6及び比較例6～8で得られた最終精製油をそれぞれ用いて、前記と同様の条件で熱分解し、得られた低級オレフィンの収率、副生重質油の生成率および連※

※続運転性の判断結果を表6に示す。

【0061】

【表6】

| | 実施例5 | 実施例6 | 比較6 | 比較7 | 比較8 |
|---------------|-------|-------|-------|-------|-------|
| 水素含有量 (wt%) | 12.71 | 12.96 | 12.08 | 11.88 | 11.69 |
| エチレン収率 (wt%) | 18.1 | 19.1 | 13.5 | 13.1 | 12.1 |
| プロピレン収率 (wt%) | 14.7 | 15.2 | 9.4 | 9.1 | 8.6 |
| 副生重質油 (wt%) | 25.0 | 23.8 | 33.2 | 35.9 | 36.1 |
| 連続運転性 | ○ | ○ | × | × | × |

【0062】本発明の実施例5～6では、溶剤抽出処理工程において重質原料油に比べて水素含有量が0.2wt%以上増加するように抽出し、続く水素化精製処理工程においてDAOに比べて水素含有量が0.5wt%以上増加するように処理しており、結果として最終精製油は、原料油に対して0.7wt%以上増加している。得られた本発明の精製油においては、いずれもNi+V濃★50

★度が0.1wtppm以下、CCRは1wt%以下、硫黄濃度は0.5wt%以下であり、高度に不純物が除去された高品質の精製油が得られている。

【0063】これに対し、溶剤抽出処理のみで精製した比較7では回収率を55%にまで低くして抽出精製しても不純物の除去が充分でないことがわかる。また、本発明の実施例6と水素化精製のみで精製した比較8とを比

較すると、水素化精製は同一条件であるにもかかわらず、不純物の除去に大きな差があることがわかり、予め溶剤抽出処理により所定の水素含有量を増加した後、水素化精製処理することにより格段に不純物が除去されて高品質の精製油が得られていることがわかる。さらに、得られた精製油を熱分解処理して低級オレフィンを製造した結果では、本発明の精製油ではエチレン収率が15%を超え、プロピレン収率は10%を超えており、さらに、副生重質油の生成状況から連続運転性は可能な範囲と判断された。一方、本発明を満足しない比較例では、エチレン収率が15%を超えておらず、さらに、副生重質油の生成量が多く連続運転性はいずれも問題があることがわかる。

【0064】実施例10

重質原油を出発ベースとした精製油の製造

*

| | 原料油1 | | | 原料油2 | 原料油 (1+2) |
|-------------------|-------|-------|-------|-------|------------------|
| | 常圧残油 | DAO | 精製油10 | GO | 精製油 10:20, GO:10 |
| 得率 (wt%) (原油=100) | 61 | 49 | 45 | 18 | 30 |
| 水素含有量 (wt%) | 11.20 | 11.42 | 11.95 | 13.70 | 12.53 |
| 水素含有量増加量 (wt%) | — | 0.22 | 0.53 | — | — |
| 合計水素増加量 (wt%) | — | — | 0.75 | — | — |
| V+Ni (wt ppm) | 153.0 | 14.2 | 0.7 | <0.1 | <0.1 |
| アスファルト質残留炭素 (wt%) | 12.50 | 3.60 | 1.90 | 0.00 | 1.20 |
| S (wt%) | 4.70 | 3.50 | 0.40 | 0.05 | 0.27 |
| エチレン収率 (wt%) | — | — | — | — | 17.6 |
| プロピレン収率 (wt%) | — | — | — | — | 14.1 |
| 副生重質油 (wt%) | — | — | — | — | 25.8 |
| 連続運転性 | — | — | — | — | ○ |

【0066】実施例10では、残渣油を原料油として、本発明の精製処理を施して得られた精製油に、別途調製した不純物濃度が低い留出油を混合して低級オレフィン製造用原料としたものであり、エチレンおよびプロピレンの収率、連続運転性のいずれも満足できる結果であることを確認できた。

【0067】

【発明の効果】本発明の精製方法を用いれば、水素含有※

* API比重27.4のアラビアンヘビー原油を蒸留により留出油と残渣油に分離し、留出油の一部を水素化精製してGOを得た。一方、残渣油であるAPI比重10.9の重質油を原料油1として、本発明の実施例1と同様の条件で溶剤抽出処理と、水素化精製処理とを実施して精製油10を得た。この精製油10の一部（原油100重量部に対して20重量部）と上記GOを原料油2との一部（原油100重量部に対して10重量部）を混合し、低級オレフィン製造用熱分解原料として用い、低級オレフィンを製造した。実施例10の常圧残油、脱アスファルテン油、水素化精製脱アスファルテン油及び重質エチレン原料の得率、水素含有量、Ni+V金属含有量、CCR含有量、及びS含有量を表7に示す。

【0065】

【表7】

※量が12wt%以下の重質油を、確実にかつ経済的に精製して不純物を低減した精製油を得ることが可能となり、従来限定されて重質油の用途が大幅に拡大させることができる。また、本方法で得られた精製油を低級オレフィン製造用原料として用いた場合には、エチレンおよびプロピレンを経済的に見合う収率で製造することができ、さらに、連続運転性に関しても商業運転が可能な範囲とすることができるものである。

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